CHAPTER ONE

Managing cadmium in agricultural systems

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Abstract

Cadmium (Cd) is a naturally occurring element present in all soils from both geogenic and anthropogenic sources. The primary risk pathway to humans is exposure through dietary intake in foods and by inhalation through smoking, with the target affected organ being the kidney. In developed countries, Cd intakes by populations are below levels of concern as determined by the World Health Organization. However, in some developing countries Cd intakes are increasing, so management of Cd transfer through the food chain remains important to minimize human exposure.

Significant advances have been made in understanding the behavior of Cd in agricultural systems and a range of management options are now available for farmers to minimize uptake into crops and forages. Our understanding of the genetics of root Cd uptake, translocation and accumulation in shoots, grains and tubers has advanced significantly and farmers now have the option to manage Cd through choice of crop and/or new low-Cd cultivars. High-risk soils can now be identified by soil testing and various agronomic options are available to minimize plant uptake on these high-risk soils. Combined, these management options can rapidly reduce Cd concentrations in foods, quicker than reductions in Cd inputs in fertilizers, manures or atmospheric sources. However, it is important that we limit Cd accumulation in soils and aim for zero-net accumulation. Calculating limits to Cd inputs necessary to achieve this are compromised by the lack of accurate information on measurement of rates of Cd leaching under field conditions.

1. Introduction

Cadmium (Cd), a metal in Group IIB of the periodic table with no known essential functions in terrestrial plants or animals, is a naturally occurring element in all rocks, soils and waters. Cadmium is enriched in certain ores—principally copper (Cu), zinc (Zn) and lead (Pb) sulfides. Cadmium is produced industrially as a by-product of the Zn smelting industry, and historically found uses in batteries, semiconductors, electroplating, and stabilizers, although industrial use has been restricted in many countries due to human and environmental health concerns.

Concerns for the effect of Cd on human health date back to the mid-19th century (Sovet, 1858) not long after the identification of Cd as a distinct element in 1817 (Robards and Worsfold, 1991). The toxicity of Cd to humans was first observed in occupational exposures (inhalation of fumes or dusts) (Friberg, 1948) but the possible link between dietary intake of Cd and accumulation of Cd in humans was first postulated by Schroeder and Balassa (1961). Subsequently, these authors reported a link between Cd concentrations in phosphatic fertilizers and Cd accumulation in vegetables (Schroeder and Balassa, 1963). Later that decade the widespread expression of Cd toxicity, as itai-itai disease (osteomalacia—bone disease), in residents of the Toyama Prefecture in Japan was found to be the result of ingestion of rice contaminated by Cd from polluted irrigation waters. In 1968 the disease was declared by the Japanese government to be the result of environmental Cd pollution (Kobayashi, 1978; Nordberg, 2009). In 1972 the World Health Organization (WHO) set a provisional tolerable weekly intake (PTWI) for Cd (WHO, 1972) and since then, Cd has become an element of increased scrutiny in the food chain.

Cadmium is naturally present in all soils but concentrations in soil may be elevated due to addition of agricultural inputs to soil, or due to pollution of soils by disposal or reuse of industrial or urban wastes. Since the 1970s, many studies have examined the food chain transfer of Cd in agricultural systems, evaluating the sources of Cd in soils, behavior and mobility of Cd under different soil physicochemical conditions, uptake and translocation by plants and agronomic management to limit crop and animal accumulation of Cd. This review aims to examine these aspects of Cd transfer through the food chain with a view to outlining the best management practices to mitigate Cd transfer from soils to crops.

1.1 Cadmium as a human health issue

Cadmium is a non-essential element for humans that is almost absent from the body at birth and accumulates with age in the kidney and liver to peak at around age 50 (Schroeder and Balassa, 1961; WHO, 1972). The primary routes of intake by humans are through the diet and by smoking (Järup, 2003). Most of the Cd absorbed by the human body is excreted, but between 5% and 10% is retained, mostly (>50%) in the kidneys (WHO, 2011). It is clear from occupational exposures to Cd that this element is highly toxic to humans (Friberg, 1948), and that high dietary exposure also leads to severe toxicity (Kobayashi, 1978). Damage to the kidneys occurs when the Cd concentration in the renal cortex exceeds approximately 200 mg kg^{-1} (wet weight), as evidenced by excretion of proteins (proteinuria) and calcium

(Ca). The latter leads to osteomalacia which is the underlying cause of itai-itai disease (Kobayashi, 1978). Cadmium has also been classified by the International Agency for Research on Cancer (IARC) as carcinogenic to humans (Group 1), causing lung cancer and also because there is some evidence for links to kidney, liver and prostate cancer (IARC, 2018). However, most of the evidence for cancer is derived from high occupational exposures to Cd through inhalation rather than low level intake through food consumption. Several extensive reviews have been published examining and describing the toxicity of Cd to humans which the reader is referred to (Godt et al., 2006; Nordberg, 1974, 2009; Satarug et al., 2003, 2010).

The Food and Agriculture Organization of the United Nations (FAO) and WHO, through the Joint Expert Committee on Food Additives (JECFA), reviewed toxicological and epidemiological information on Cd in the 1970s and set a PTWI for human Cd intake in 1972 that is equivalent to a daily intake of 1 μg Cd kg body weight^{-1} which was based on limiting kidney cortex Cd concentrations to 50 mg kg^{-1}, a Cd absorption rate of 5% of intake and a daily excretion of 0.005% (WHO, 1972). Subsequently, many jurisdictions around the world set maximum concentrations for Cd in foodstuffs in order to limit Cd intake of their populations to less than the PTWI. Many jurisdictions now monitor Cd concentrations in foodstuffs and participate in the Global Environmental Monitoring System, established by WHO in 1976 to monitor levels and trends of contaminants in food, their contribution to total human exposure, and significance with regard to public health and trade.[a] Intakes of Cd are generally greater in countries where rice is a staple food item, due to higher Cd concentrations in rice grains than other staples, and possibly lower concentrations of iron (Fe) and Zn—this is discussed further below. While in developed countries the dietary intakes of Cd have generally reduced due to stricter controls on Cd emissions to the environment (Nordberg et al., 2007), in some developing countries it is concerning to note that human Cd intakes are increasing (Fig. 1) (Song et al., 2017; Wang et al., 2017).

Since the initial studies in Japan on itai-itai disease, there has been extensive research examining the factors that affect absorption of Cd by the human body (Anderson et al., 1992; Reeves et al., 2001; Reeves and Chaney, 2008) and it is now recognized that itai-itai disease was exacerbated by a subsistence rice-based diet deficient in other essential nutrients such as Fe and Zn which reduce Cd bioavailability to humans (Chaney, 2015; Chaney et al., 2004).

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[a] https://extranet.who.int/gemsfood/

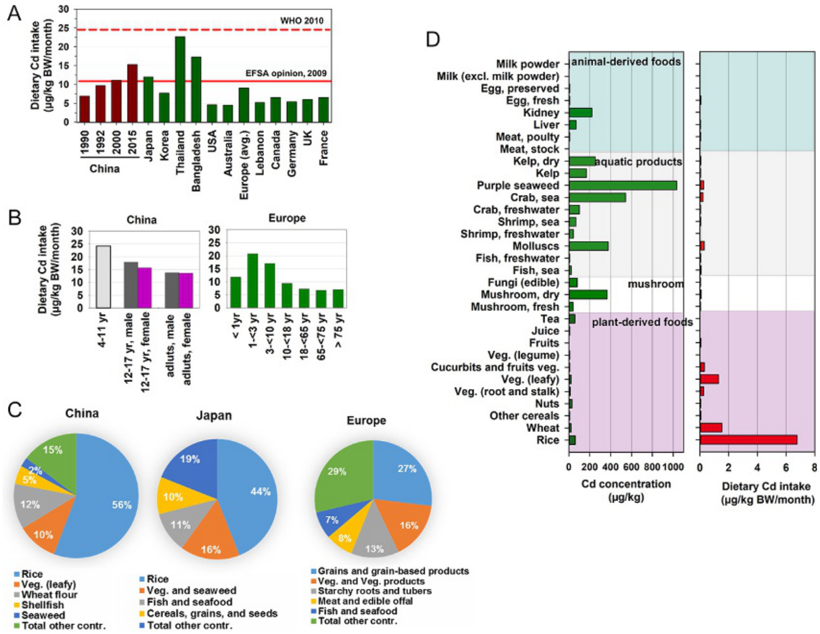

Fig. 1 Human dietary Cd exposure. (A) Dietary Cd intake levels in different countries and recommended provisional tolerable monthly intake limits, (B) dietary Cd intake as divided by age groups in China and Europe, (C) main contributions of dietary Cd intake for Chinese, Japanese and European populations, and (D) the concentrations of Cd in foods and their contributions to dietary Cd intake for the Chinese population. *From Wang, P., Kopittke, P.M., McGrath, S.P., Zhao, F.J., 2017. Cadmium transfer from soils to plants and its potential risk to human health. In: Singh, B.R., McLaughlin, M.J., Brevik, E. (Eds.), The Nexus of Soils, Plants, Animals and Human Health. Catena-Schweizerbart, Stuttgart, Germany, pp. 138–147 with permission, available at www.schweizerbart.de/9783510654178.*

Other populations with high Cd intakes due to ingestion of nonrice-based diets grown on soils or foods enriched in Cd often show no increased morbidity despite exhibiting levels of biomarkers suggesting high Cd exposures (Burbure et al., 2003; McKenzie-Parnell et al., 1988; McKenzie-Parnell and Eynon, 1987; Sharma et al., 1983; Strehlow and Barltrop, 1988; Wright et al., 2010).

Despite a recognition that rice-based diets pose unique risks in terms of Cd intake, a separate evaluation of Cd risks to human health in Europe, conducted by the European Food Safety Agency (EFSA), suggested a much lower tolerable weekly intake, 2.5 µg Cd kg body weight^{-1} should be used to limit Cd intake by highly exposed individuals (EFSA, 2009a, 2011; Heppner et al., 2009). However, subsequent international review of the

PTWI by WHO in 2010 did not adopt this lower permissible intake figure, and recommended a provisional tolerable monthly intake (PTMI) limit, rather than a weekly intake limit, of 25 μg Cd kg body weight^{-1}. This limit is equivalent to 0.83 μg Cd kg body weight^{-1} day^{-1}, i.e. only slightly lower than the 1.0 μg Cd kg body weight^{-1} day^{-1} limit set 1972 and well above the EFSA suggested weekly limit that is equivalent to a daily limit of 0.36 μg Cd kg body weight^{-1} day^{-1}. Recent estimated average dietary intake values are below the WHO 2010 limit but exceed the EFSA limit in several countries (Fig. 1).

Chaney (2015) argued that risks to human health from ingestion of Cd in foods are overestimated due to the bioavailability of food Cd being much lower than Cd in subsistence rice-based diets, and the lack of evidence of kidney dysfunction at levels much higher than the EFSA tolerable weekly intake (Ezaki et al., 2003; Ikeda et al., 2006). However, to date, food Cd standards internationally are not based on any assessment of bioavailability, but only on total Cd concentrations.

While there may be conflicting views on the dangers to human health presented by food Cd, it is pertinent to note that the WHO examined the major risks globally to human health, and food contamination (by any element) did not appear in the top 20 risks. In terms of food quality, only micronutrient deficiencies in food (iodine, Fe and Zn) were identified as important global risks to human health (WHO, 2009).

1.2 Cadmium as a trade issue for food commodities

Many countries have established limits for Cd in foods based on the WHO tolerable intake values including China, European Union (EU) countries, Australia, New Zealand and others (Clever and Jie, 2014; EU, 2006; FSANZ, 2011; WHO, 1972, 2011)—a selection of food limits is given in Table 1. There are no food Cd standards in USA[b] although the US Food and Drug Administration monitors Cd concentrations in infant/toddler foods[c] and compares these to international food standards set by the WHO and the United Nations Food and Agriculture Organization (FAO) through the Codex Alimentarius Commission. The Codex Alimentarius Commission sets international standards for Cd to protect consumer health and facilitates fair international trade in food commodities. Codex standards are recognized by the World Trade Organization as international reference standards for

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[b] https://www.atsdr.cdc.gov/csem/csem.asp?csem=6&po=7

[c] https://www.fda.gov/food/metals/combination-metals-testing

Table 1 A non-exhaustive list of Cd thresholds and limits in the environment.

Compartment	Unit	Limit	References
Body burden Urinary threshold	μg Cd g^{-1} creatinine	2.0[a]	Effect level (ECB, 2007)
		3.9[b]	Effect level (EFSA, 2009b)
		5.2	Effect level (WHO/FAO/JECFA, 2011)
Diet Tolerable daily intake for 70 kg adult	μg Cd day^{-1}	25	EFSA opinion[c] (EFSA, 2009b)
		58	WHO/FAO/JECFA (2011)[d]
		70	WHO 1989–2009* (WHO, 1989)
Food limits (fresh wt. basis) Wheat grain	mg Cd kg^{-1}	0.10	China: GB 2762-2017 (CFDA, 2017)
		0.20	Codex Alimentarius (FAO, 2015)
		0.20	EC No. 1881/2006 (EU, 2006)
Rice	mg Cd kg^{-1}	0.20	EC No. 1881/2006 (EU, 2006)
		0.20	China: GB 2762-2017 (CFDA, 2017)
		0.40	Codex Alimentarius (FAO, 2015)
Potato	mg Cd kg^{-1}	0.05	Codex Alimentarius (FAO, 2015)
		0.05	China: GB 2762-2017 (CFDA, 2017)
		0.10	EC No. 1881/2006 (EU, 2006)
Chocolate products 30–50% dry cocoa solids	mg Cd kg^{-1}	0.30	EC No. 488/2014 (EU, 2014)
≥50% dry cocoa solids		0.80	EC No. 488/2014 (EU, 2014)
50–70% dry cocoa solids		0.80	Codex Alimentarius (FAO, 2018)
≥70% dry cocoa solids		0.90	Codex Alimentarius (FAO, 2018)

Continued

Table 1 A non-exhaustive list of Cd thresholds and limits in the environment.—cont'd

Compartment	Unit	Limit	References
P fertilizer limits	mg Cd kg^{-1} P_2O_5		Ulrich (2019)
		21	Switzerland
		46	Norway
		60	Europe
		146	Japan
		400	California
Biosolid limit	mg Cd kg^{-1} dry matter	10	Victoria (2004a, 2004b)
		15	China GB 4284-2018 (China National Standardization Administration, 2018)
		20	South Australia (2017)
		20	Western Australia (WA DEC, 2002)
		20	EU Directive 86/278/EEC (EU, 1986)
		85	USEPA 503 (USEPA, 1993)
Residential soil clean-up limits	mg Cd kg^{-1}		Provoost et al. (2006)
		0.4	Sweden
		3.0	Norway
		20	Germany
		37	USA

[a] Effect level of 2.00 μg g^{-1} divided by a margin of safety of 3.

[b] Effect level of 3.9 μg g^{-1} divided by 3.9 accounting for inter-individual variation.

[c] Opinion of the European Food Safety Authority (EFSA) defined as 2.5 μg Cd $week^{-1}$ kg^{-1} body weight and converted here for an adult of 70 kg.

[d] Adopted in the 73rd meeting of the Joint FAO/WHO Expert Committee on Food Additives (JECFA) June, 2010 and defined as a provisional tolerable monthly intake (PTMI) of 25 μg kg^{-1} body weight and converted here for an adult of 70 kg.

[e] Provisional tolerable weekly intake of 7 μg Cd kg^{-1} body weight and converted here for an adult of 70 kg.

the resolution of disputes concerning food safety and consumer protection.[d] Thus Codex standards for Cd in foods are the *de facto* international Cd standards for trade in food commodities (CODEX, 2019) and are therefore used in disputes regarding restrictions to trade of commodities based on Cd content. Cadmium concentrations in produce have, in several instances, led to restrictions in trade of foods (Eugenio Figueroa, 2008). Recently, EFSA enacted (in January 2019) more restrictive changes to permissible concentrations of Cd in cocoa and cocoa products (EU, 2014) on the basis of the revised risk assessment for Cd uptake in the EU (EFSA, 2009a), which has created significant trade concerns for several cocoa-exporting countries.[e] EFSA has also foreshadowed lowering of the permissible levels of Cd for other foods, and has recommended a progressive implementation by EU farmers and food business operators of Cd reduction measures.[f]

Clearly, irrespective of the level of risk posed by food Cd to human health, concentrations of Cd in foodstuffs are important in relation to trade of food commodities and are the subject of disputes regarding restrictive trade rules under the World Trade Organization's jurisdiction. Hence it is prudent that agricultural systems be managed to limit Cd accumulation in soil, and to utilize agronomic and genetic management to minimize Cd uptake by crops and animals prone to Cd accumulation.

1.3 Current legislation controlling cadmium in the environment

The potential adverse effects on human health are relatively more critical than are the ecotoxic effects of Cd on soil ecosystems or indirect effects from soil Cd affecting aquatic ecosystems (Chaney, 1980; McGrath, 1997; Smolders and Mertens, 2013). Therefore, Cd emissions and Cd concentrations in the environment are mainly regulated to limit the risk to humans through food ingestion, and various thresholds or legal limits have been defined at all levels in the soil-food-human exposure chain. Before proceeding to a table of the current Cd legislation, a conceptual figure (Fig. 2) is made on the various steps at which one can regulate food chain risk and which may explain the divergence of Cd limits across various jurisdictions.

As noted earlier, the target organs for adverse effects of Cd on human health are the human bone and kidney, depicted on the right-hand side in

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[d] https://www.who.int/foodsafety/areas_work/food-standard/general_info/en/index2.html

[e] https://ictsd.iisd.org/bridges-news/bridges/news/eu-regulation-on-cadmium-in-chocolate-fuels-wto-debate-on-health

[f] https://ec.europa.eu/food/safety/chemical_safety/contaminants/catalogue/cadmium_en

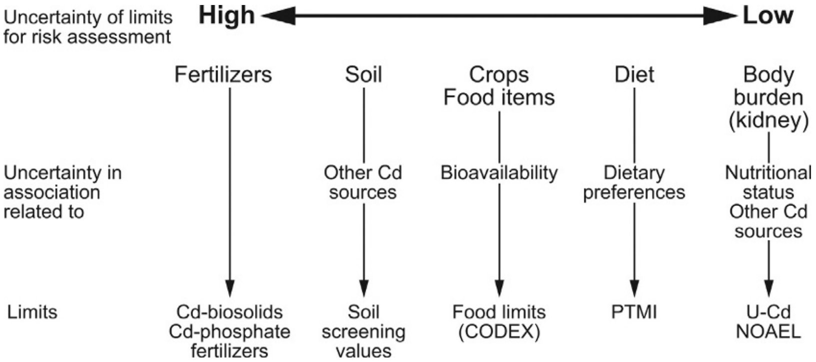

Fig. 2 Risk assessment of Cd is made at various levels in the chain between the fertilizers and humans. The Cd limits that have been derived have a larger uncertain relationship with the risk as they move away from the target, i.e. uncertainty increases from right to left. SSV, soil screening values (soil Cd limits); PTMI, provisional tolerable monthly intake; U-Cd NOAEL, urinary Cd no observed adverse effect level. *Adapted from Smolders, E., 2017. Scientific Aspects Underlying the Regulatory Framework in the Area of Fertilizers—State of Play and Future Reforms. Brussels, Belgium.*

Fig. 2. Experimental and epidemiological studies have led to chronic effect thresholds for Cd in the kidney that differ by a factor of about 2.5 among various assessments (Table 1). This variability is relatively low when compared with the limits derived to regulate Cd emissions to the environment in various jurisdictions. For example, there is a factor 20 difference in Cd limits in phosphorus (P) fertilizers (Table 1) even though these limits are in principle also derived to protect human health, i.e. kidney function. The variability of these limits grows when moving away from the target, that is moving from right to left in Fig. 2 and moving to soil limits or to Cd emission standards. This trend in increasing divergence of limits is logical because of increasing uncertainty and variability; there is variability in the transfers of environmental Cd between the compartments and there are other sources of Cd not included in the most dominant pathway shown in Fig. 2. For example, the body burden of Cd is the result of exposure from food, the main source, but there is also Cd exposure via drinking water, inhalation and smoking. There is no unique relationship between daily dietary Cd intake and body burden, partly because of these other sources of Cd but also because nutritional status, mainly Fe and Zn status, also affects the systemic Cd uptake by humans, i.e. the food to human transfer.

This leads to various assumptions in modeling the diet to the body burden and, hence, the dietary limits vary somewhat more than the limits on the target organ. The same is true for food limits that are, in turn, derived from modeling the food to diet transfer, for the soil limits that are estimated with soil-to-food transfer models and for emission limits that are estimated with mass balance models to meet soil limits, and so on. This means that the extreme variability in Cd limits across jurisdictions for soils or farm inputs does not necessarily relate only to political aspects or to different risk perception; risk assessment is increasingly dependent on assumptions when moving further away from the target effect. Table 1 gives a non-exhaustive set of limits or thresholds sorted by the various compartments. Several of the thresholds are recommended ones with no legal basis, for example body burden and dietary limits (PTMI) are derived by scientists in risk assessment or by overarching organizations such as WHO, the FAO or, in Europe, the EFSA. These limits are not imposed as legal limits in nations (excluding occupational limits) but are used to infer limits in food, environmental compartments and in emissions, each of these latter can have a legal basis.

The selected food limits collated here refer to the FAO Codex limits, the European regulations (EU, 2006) and the Chinese regulations. One does not notice a consistent difference in conservatism among these three main regulations. These regulations vary over time in the jurisdictions, sometimes in a rather inconsistent manner. For example, the wheat Cd regulation has become less stringent in Europe (grain limit increased from 0.1 to 0.2 mg Cd kg^{-1}) while the tolerable daily intake was revised and lowered around the same time by EFSA. Clearly, practical considerations are often at stake. As noted earlier, a new set of EU food regulations for Cd appeared recently for cocoa which initiated many new projects to study Cd in a crop that had not received much attention previously. The new cocoa limits refer to Cd concentrations in the final product, not in the bean and the limits depend on the cocoa content of the product.

On July 2, 2018, the Codex Alimentarius Commission has also defined, for the first time, limits for Cd in chocolate. The State of California has agreed in February 2018 on even stricter Cd limits for chocolate products under Proposition 65, above which consumers will be warned of the potential health risks. With the recent adoption of these limits by Codex, it is foreseeable that several other countries will follow soon. The chocolate limits in Europe have been derived because Cd exposure is exceeded more readily in children and chocolate is an important vector of Cd intake for children. The Cd-related health risks related to eating chocolate have, so far, never been demonstrated.

The consequences of the chocolate limits mainly affect the single origin chocolates from South America where soil Cd is naturally high and from which single origin dark chocolate now cannot be produced (given the new cocoa Cd limits) for over half of the production in Ecuador and Colombia (Arguello et al., 2019).

The P fertilizer limit in Europe, i.e. 60 mg Cd kg^{-1} P_2O_5 (equivalent to 137 mg Cd kg^{-1} P), was concluded in 2019 after more than 20 years of debate. That limit is expected to affect about 8% of the mineral P fertilizer sold on the European market (Smolders, 2017). The limits came into force to harmonize the discrepant regulations within Europe that violated free trade; for over a decade several countries were granted derogations to use their national Cd limits. The new limit of 2019 is based on the "stand still principle" or "zero net accumulation" (Witter, 1995), not on health risk assessment and several member states had claimed to have local soil, climate, land use or crop use conditions that justified their national limit. There have been several EU-wide approaches to model the mass balance of Cd in agricultural soils (Römkens and Smolders, 2018; Six and Smolders, 2014)—details of these balances are given later in this review (Section 5.2).

The most recent EU-wide mass balance was made at a 1 km × 1 km scale, implemented in a geographic information system (GIS) and national mean mass balances and model uncertainty assessments were included. That analysis showed that the projected EU-wide mass balance over 100 years is now close to a zero net accumulation. Most importantly, the error propagation showed no statistically significant effect of the Cd concentration in the P fertilizer (between 20 and 60 mg Cd kg^{-1} P_2O_5) on the change in the Cd mass balance in most, but not all, countries, i.e. the uncertainty of the mass balance model was too large to identify the true EU-wide limit that would lead to zero net accumulation. That scientific result was obviously not given any weight in the final policy debates and decision. Several parties have shown their dissatisfaction with the outcome or with parts of the modeling (Sterckeman et al., 2018, 2019; Ulrich, 2019). At the current EU limit in fertilizers and at an annual dose of 50 kg P_2O_5 ha^{-1} yr^{-1} (above average P application), the equivalent annual dose of Cd is 3 g Cd ha^{-1} yr^{-1}. That dose is small compared to the lowest tolerated Cd loading rate via biosolids (sewage sludge) in various jurisdictions (30 g Cd ha^{-1} yr^{-1}, see below). In many other countries outside Europe, Cd regulations in mineral fertilizers are also in place, some of these being voluntary.

The biosolid limits for Cd vary over a factor 8 among jurisdictions (Table 1). The biosolid limits are here expressed as the Cd concentrations in the biosolid. Most jurisdiction have an additional limit value based on total loading rate expressed as g Cd ha^{-1} yr^{-1} (annual, cumulative or 5 year average) or on a soil Cd concentration limit. The loading rates of Cd via biosolids vary markedly: they are 30 g Cd ha^{-1} yr^{-1} in three Australian states

(WA, VIC, SA), 150 g Cd ha^{-1} yr^{-1} in the EU directives and 1900 g Cd ha^{-1} yr^{-1} in the US-EPA 503 regulation. The rather liberal US-EPA regulations were received by much controversy at the time (McBride, 1995). Within Europe, the biosolid limits of European nations can be lower but never higher than the EU directives mentioned in Table 1.

The soil clean-up limits given in Table 1 are merely illustrating the even larger divergence in limits compared to the fertilizer or biosolid limits. This list is certainly not exhaustive (see Carlon (2007) for a comprehensive list for the EU) but shows that the risk assessment of Cd in soil is open to numerous assumptions about land use, fraction of food derived from that land, various protection goals, etc. (Provoost et al., 2006).

2. Sources of cadmium in agricultural systems

2.1 Geogenic sources

As noted earlier, Cd is naturally present in all rocks and hence in all soils. Krauskopf and Bird (1995) ranked Cd 64th in crustal abundance among the elements (Krauskopf and Bird, 1995). The concentrations of Cd in rocks vary widely with igneous and metamorphic rocks generally having lower Cd concentrations than sedimentary deposits (Kabata-Pendias, 2010). Cadmium is often enriched in soils developed on sedimentary phosphatic rocks (Garrett et al., 2008) due to the high concentrations of Cd in many sedimentary phosphates (McLaughlin et al., 1996). Geogenic soil Cd concentrations can vary from <0.01 mg kg^{-1} up to tens or hundreds of mg/kg where soils develop on carbonates, shales or phosphorites (Canty et al., 2014; Garrett et al., 2008; Jyoti et al., 2015; Khan et al., 2010; Kim and Thornton, 1993; Lalor, 2008; Lalor et al., 1998; Liu et al., 2017; Lund et al., 1981; Quezada-Hinojosa et al., 2009). Weathering of high-Cd parent rock material slowly releases Cd from mineral lattices to more soluble forms in soil—Cd in soil solution and weakly sorbed to mineral and organic matter surfaces (Robson et al., 2014).

It is difficult to separate geogenic from anthropogenic Cd in soils—often surface enrichment of Cd in topsoils is assumed to occur because of additions from the atmosphere and farm inputs, but this is a false assumption as biological cycling of Cd brings Cd from subsoils into topsoils (Reimann et al., 2019). Natural abundance isotopic data on Cd cycling in agricultural soils also suggests biological cycling of subsoil Cd to topsoils by vegetation (Imseng et al., 2018). Continental-scale mapping of soil Cd concentrations reveals that, even in Europe with intensive use of fertilizers and urban wastes and manures, soil Cd concentrations at the continental scale are governed more by geology than by anthropogenic inputs (Birke et al., 2017) (Fig. 3).

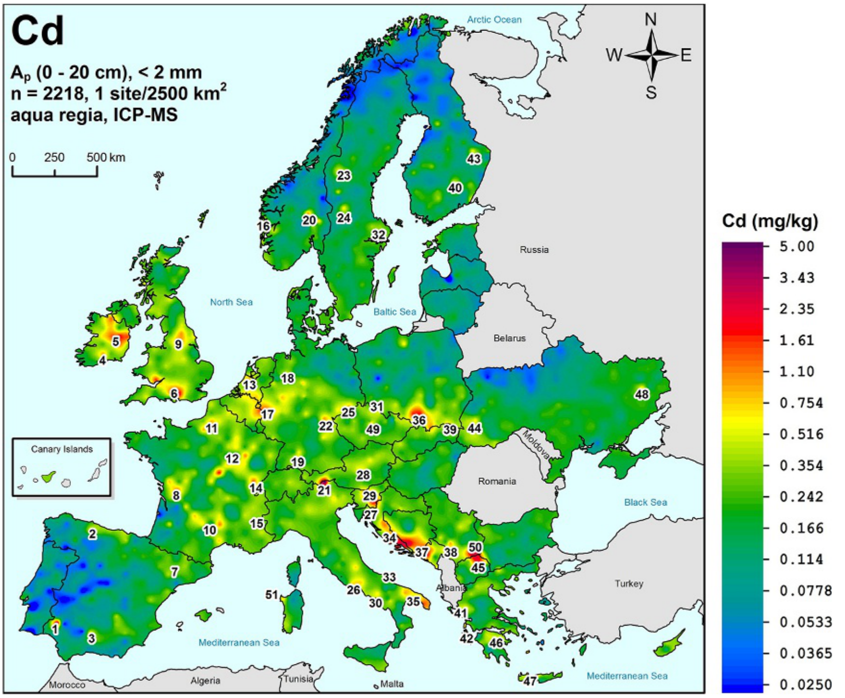

Fig. 3 Distribution of Cd in European agricultural soils. *From Birke, M., Reimann, C., Rauch, U., Ladenberger, A., Demetriades, A., Jähne-Klingberg, F., Oorts, K., Gosar, M., Dinelli, E., Halamić, J., 2017. GEMAS: cadmium distribution and its sources in agricultural and grazing land soil of Europe—original data versus clr-transformed data. J. Geochem. Explor. 173, 13–30, with permission.*

Birke et al. (2017) argue that the southern limit of the Quaternary glaciation in Europe is clearly seen in the distribution of Cd in soils separating the young soils of northern Europe from the older soils from southern Europe. Many of the high Cd soils are linked to geogenic sources evidenced by principal component analysis using other elemental ratios.

Hence, geogenic Cd may be the major stock of Cd in many soils, even those receiving Cd input from fertilizers or animal manures/biosolids. Management of this Cd is more problematic than anthropogenic Cd as the enrichment is not necessarily restricted to surface horizons and deeper strata may provide significant Cd supply to crops dependent on rooting depth.

2.2 Anthropogenic sources

The geogenic stock of Cd in a mixed plow-layer of an agricultural soil is equivalent to 300–1500 g Cd ha^{-1} for a soil with a geogenic background

Cd concentrations of 0.1–0.5 mg Cd kg^{-1} soil (Section 2.1). That stock of Cd is, and has been, enriched with anthropogenic Cd with annual addition fluxes ranging approximately 0.1–10 g Cd ha^{-1} yr^{-1}, these fluxes will be discussed in this section and in Section 5 on mass balances.

The most important anthropogenic sources of Cd into the soil are derived from atmospheric deposition, and from the applications of mineral and organic fertilizers, i.e. mineral phosphate fertilizers, biosolids, composts and manures. A significant fraction of Cd in biosolids, composts and manures may originate from crops that took up Cd from soil and, hence, the application of these materials are only net enrichments at a large scale if the Cd originates from anthropogenic additions such as feed additives for manure or industrial sources for biosolids.

Cadmium is mainly produced as a by-product from mining and extracting Zn ore minerals, particularly sphalerite (ZnS). A small amount of the total Cd supply worldwide is obtained from recycling nickel-cadmium batteries. About 25,000 Mg of Cd were produced in 2017 (excluding US production from which data are not disclosed) with China and the Republic of Korea the largest producing countries (USGS, 2019). Over 80% (2010) of the Cd produced is used for the manufacture of batteries.[g] The use of Cd in other applications such as alloys, pigments, coatings, stabilizers for plastic have decreased, particularly in Europe due to the application of strict legislation that bans the use of Cd. In contrast, the consumption of Cd in China has steadily increased in the last decades owing to its economic and industrial development. An analysis of flows and stocks of Cd in the industry in China over the period 1990–2015 concluded that Cd consumption for Ni-Cd batteries peaked in 2008 but it reduced to 84% of that peak by 2015 due to changes in market demand and local governmental policies (Shi et al., 2019). Nevertheless, at the same time the consumption of Cd in plastics increased by approximately 81%.

2.2.1 Atmospheric inputs

Cadmium is emitted to the atmosphere from natural sources, mainly volcanic emissions and from anthropogenic sources. Worldwide 85%–90% of total atmospheric Cd emissions arise from anthropogenic sources, mainly from fossil fuel combustion, nonferrous metal manufacturing, iron and steel production, cement production, and waste incineration (Alloway and Steinnes, 1999; WHO, 2000). Most of Cd in the air is associated with

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[g] International Cadmium Association, https://www.cadmium.org/introduction.

suspended particulate matter (aerosols) in the form of oxides, sulfides, sulfates and chlorides. Earlier concentrations of Cd in the air have generally been estimated to range between 0.1 and 5 $\mathrm{ng\,m^{-3}}$ in rural areas and 2 and 150 $\mathrm{ng\,m^{-3}}$ in urban and industrial areas (Alloway and Steinnes, 1999); current European mean concentrations[h] are now only 0.05 $\mathrm{ng\,m^{-3}}$. A selected ranged of atmospheric Cd deposition fluxes is presented in Table 2.

In Europe, a downward trend in Cd air concentrations has been observed in the last half century. The largest Cd emissions (2500 $\mathrm{Mg\,yr^{-1}}$) to the atmosphere were estimated to occur in the 1960s and this was the result to the growing production of nonferrous metals. However, between 1960 and 2005 emissions decreased about fivefold mainly due to the installation of more efficient flue gas desulfurization equipment in smelters and power plants (Pacyna et al., 2009). A recent emission inventory by the European Environment Agency (EEA, 2019) reported that Cd emissions in EU-28 countries declined by 64% between 1990 and 2017 (from 191 to 68 $\mathrm{Mg\,yr^{-1}}$), with Germany and Poland the EU countries having the highest contribution to total emissions in 2017.

Airborne Cd can be deposited on the soil by dry and wet deposition, which together are referred to as total or bulk deposition. Atmospheric deposition by precipitation is the main way through which atmospheric Cd is transferred to the soil. In Europe, two sampling methods are used, i.e. bulk collectors and wet-only collectors and the wet-only collectors are being recommended in the European Monitoring and Evaluation Program (EMEP). With wet-only collectors, the sampler is only opened during rain events. The main advantage of the wet-only collectors over the bulk collectors (always open) is that re-suspended Cd, which was first deposited elsewhere, is not accounted for in the measurements. Data from selected European sampling stations showed, for example, that the Cd concentrations in precipitation in Norway decreased from a peak of 0.7 $\mathrm{\mu g\,Cd\,L^{-1}}$ in the early 1980s to <0.1 $\mathrm{\mu g\,Cd\,L^{-1}}$ in 2004; similar trends were observed in the stations of Germany, Netherlands and Great Britain (Pacyna et al., 2009). By 2016, Cd concentrations in precipitation measured in 36 monitoring sites following the EMEP's atmospheric monitoring program ranged between 0.01 and 0.05 $\mathrm{\mu g\,Cd\,L^{-1}}$, with highest levels observed in Slovakia, France, Spain and Sweden (Ilyin et al., 2018). Six and Smolders (2014) calculated that the wet deposition of Cd in the EU in 2010 ranged between 0.1 and 1.0 $\mathrm{g\,Cd\,ha^{-1}}$ in the different member states with an average of 0.35 $\mathrm{g\,Cd\,ha^{-1}\,yr^{-1}}$. The most recent data

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[h] http://en.msceast.org/index.php/pollution-assessment/emep-domain-menu/comparison-menu

Table 2 Measured annual atmospheric Cd deposition fluxes, data for Europe refer to wet deposition only.

Country/City	Period	Atmospheric deposition Cd (g ha^{-1} yr^{-1})	Comment	References
South America				
Argentina/Cordova	2005–2006	1.35	Analysis by GFAAS	Bermudez et al. (2012)
Colombia/Montelibano	2010–2011	4.3	Analysis by GFAAS	Marrugo-Negrete et al. (2014)
Asia				
Korea/Chuncheon	2008–2009	0.5	Analysis by ICP-MS	Kim et al. (2012)
Northern China/ Shijiazhuang city	2007–2010	6.4	Analysis by ICP-MS, agricultural site	Pan and Wang (2015)
Northern China/Yucheng city	2007–2010	3.9	Analysis by ICP-MS, agricultural site	Pan and Wang (2015)
Northern China/ Xinglong	2007–2010	2.9	Analysis by ICP-MS, rural site	Pan and Wang (2015)
China/Guizhou, Henan, Shanxi, Fujian	2015	2.7	Analysis by ICP-MS, agro-ecosystems in four natural regions	Zhang et al. (2018)
China/Lianyuan	2015–2016	17	Analysis by ICP-MS	Liang et al. (2017)
Europe				
Europe	2017	0.16 (0.05–0.36)	Mean and range of national averages detected with ICP-MS	EMEP (2019)[a]
Oceania				
New Zealand		0.2	Analysis by FAAS and GFAAS, pasture sites	Gray et al. (2003)

[a] http://en.msceast.org/index.php/pollution-assessment/emep-domain-menu/comparison-menu.

of 2017 showed that these deposition rates have further reduced to 0.05–0.36 g Cd ha^{-1} yr^{-1} with an average of 0.16 g Cd ha^{-1} yr^{-1} (Table 2). These data are well below the Cd deposition values reported in previous literature for European soils (i.e. Nicholson et al. (2003) reported a European average of 1.9 g Cd ha^{-1} yr^{-1}).

The difference is related to the inherent decrease in atmospheric Cd emissions in Europe but also to the present use of more precise analytical instruments (inductively coupled plasma mass spectrometers—ICP-MS) with lower limits of detection for Cd and better sampling methods (Six and Smolders, 2014). Indeed, detection limits of the graphite furnace atomic absorption spectroscopy (GFAAS) instruments used before the widespread use of ICP-MS around 2000 yielded quantification limits not lower that 0.1 μg L^{-1} which, at 800 mm annual precipitation, is equivalent to 0.8 g Cd ha^{-1} yr^{-1} as the corresponding quantification limit of Cd deposition. The current ICP-MS instruments allow at least 10-fold lower detection limits, hence the EU Cd deposition data below 0.08 g Cd ha^{-1} yr^{-1} in some countries (Table 2) were not possible to detect prior to use of ICP-MS instrumentation.

Compared with the EU, less is known about the current Cd emissions in other areas of rapid urban and industrial development. Cheng et al. (2015) compiled a comprehensive atmospheric emission inventory of Cd (and other heavy metals) in China with data from 2000 to 2010. The national total emissions of Cd from anthropogenic sources followed an overall increasing trend, with an annual increase rate of 9%. The total Cd emissions in 2010 were estimated to be 800 Mg, of which the major contributions came from nonferrous metals smelting (43% of total) followed by coal combustion. Cadmium emissions are distributed principally among the eastern, central and southern regions of China in accordance with the level of energy consumption and industrial development. In that study, the calculated level of uncertainty to the estimated data was large (−15% to 48%) which highlights the need for more detailed investigations of atmospheric Cd emissions as suggested by those authors.

Measured Cd deposition data in China suggest that the atmospheric Cd deposition is significant. In the Yangtze River delta of China, the mean Cd input to agricultural land from total atmospheric deposition is 2.7 g ha^{-1} yr^{-1} (Hou et al., 2014). This value was calculated from dry and wet deposition data collected from 2007 to 2008 in 47 rural sites. Recently, Feng et al. (2019) conducted a 2-year experiment to evaluate total Cd deposition fluxes from urban, traffic and rural sites in a typical urban agglomeration in south-central China and the impact of this deposition on a paddy soil. Annual deposition fluxes were 11.4, 21.3 and 12.9 g Cd ha^{-1} for urban, traffic and rural sites, respectively. Cadmium deposition in this area are much higher than in other regions of China (i.e. Yangtze River delta) suggesting an elevated level of atmospheric contamination. Moreover, Cd annual input deposition fluxes accounted for 52–80% of the total input (fertilizer and irrigation water also considered) for the paddy soil. A comprehensive national assessment for China was made by Luo et al. (2009) who collated deposition data from 1999 to 2006 in different regions of China. The average Cd deposition was 4 g ha^{-1} yr^{-1} (relative standard deviation of 142%, range 0.4–25 g ha^{-1} yr^{-1}). That study calculated that 35% of total Cd input to agricultural soils in China is derived from atmospheric deposition. All these data of China reflect the total (dry + wet) Cd deposition and may overestimate net enrichments since dry deposition includes dust re-suspended from other soils. The above-mentioned Cd emission inventory of Cd in China, complemented with a more recent one, estimate the annual atmospheric Cd emissions in China to be between 800 and 1200 Mg Cd yr^{-1} (Cheng et al., 2015; Shi et al., 2019). These emissions, divided by the total area of China ($9.6 \times 10^6 km^2$), yields about 1 g Cd ha^{-1} yr^{-1}, which is about four times lower than the average Cd deposition reported by Luo et al. (2009), although it is unlikely emissions are evenly spread across the country. It is clear that there is a need for better estimations of the net deposition of Cd in China.

2.2.2 Fertilizers

Nitrogen, potassium and sulfur fertilizers do not contain significant amounts of Cd and therefore their contribution to Cd accumulation will be minor. In contrast, P fertilizer is a major source of Cd in agricultural systems (Andersson, 1976; McLaughlin et al., 2011; Sheppard et al., 2009). Inorganic phosphate fertilizers contain Cd that is naturally present in the phosphate rock, the raw material for its production. The concentration of Cd in phosphate rock varies widely and is related to the type of ore (igneous or sedimentary) and geographic provenance. It is well established that phosphate from igneous deposits contain low Cd concentrations (range <1–4 mg Cd kg^{-1}) and such deposits are located in South Africa and Russia. Higher Cd concentrations (range <1–150 mg Cd kg^{-1}) are reported in phosphate rock from sedimentary deposits derived from Morocco, Togo, Senegal and Idaho, USA (McLaughlin et al., 1996; Roberts, 2014). Currently, most of the mined phosphate rock is extracted from sedimentary rocks and its main use is the production of phosphoric acid, which is the precursor for the manufacture of high analysis fertilizers, i.e. ammonium phosphates (Van Kauwenbergh, 2010).

During the production of phosphoric acid, only a small fraction of Cd from the phosphate rock is removed to the gypsum by-product. Cadmium remains associated to the phosphate and therefore the Cd/P ratio in the final fertilizer product reflects that in the rock phosphate. Cadmium concentrations in fertilizers are usually expressed on a unit P basis. Table 3 collates data of different surveys of such concentrations. Because phosphate fertilizers are considered the major source of Cd in European agricultural soils (Six and Smolders, 2014), extensive surveys of Cd (and other trace metals) have been conducted in commercially available mineral phosphate fertilizers (pure and blended) that are sold in Europe. For example, Nziguheba and Smolders (2008) collected 196 fertilizer samples from 12 EU countries and determined that the Cd concentrations ranged from <0.2 to 275 mg Cd kg^{-1} P, with a mean of 82.7 mg Cd kg^{-1} P. Furthermore, a significant and positive correlation between the concentrations of Cd and P in the fertilizers was also observed (Fig. 4), which confirms that phosphate rock is the source for this contaminant as indicated in earlier reviews, i.e. McLaughlin et al. (1996).

Recently, a more extensive survey ($n=414$) of phosphate fertilizers from 28-EU countries + Norway was conducted in which the number of samples collected in each country was proportional to their consumption of P. Marked differences were observed in the mean Cd/P ratios among countries, with largest mean values determined in Poland, Portugal, Spain and the UK and lowest values in Estonia, Finland, Romania and Sweden. The sample mean Cd concentration was 62 mg Cd kg^{-1} P and the consumption-based weighted mean 73 mg Cd kg P^{-1} (Fig. 5) (Verbeeck et al., 2020).

The values reported in both European surveys were in the same range as the data reported by Smidt et al. (2012) for fertilizers in Germany ($n=78$, range 0.55–245; mean 108 mg Cd kg^{-1} P) and Brazil ($n=39$, range 6.4–433; mean 141 mg Cd kg^{-1} P). Another small collection of 41 samples of Iranian fertilizers determined their mean concentration was 35.5 mg Cd kg^{-1} P (Latifi and Jalali, 2018). In a small worldwide survey ($n=36$) of phosphate fertilizers used in tobacco, Cd concentrations ranged from 0.2 to 223 mg Cd kg^{-1} P, with mean value of 54 mg Cd kg^{-1} P (Lugon-Moulin et al., 2004). In a survey of 151 P-containing fertilizers used in China, Cd concentration ranged from trace levels to 165 mg Cd kg^{-1} P, with a mean of 9.2 mg Cd kg^{-1} P and 90% of the samples containing <23 mg Cd kg^{-1} P, indicating

Table 3 Recent data for total Cd concentrations (mg Cd kg^{-1} P) in phosphate fertilizers outside Europe.

Country	Fertilizer type	Mean (mg Cd kg^{-1} P)	Range	Comment	Reference
Iran	NPK[a]	41.9	–	$N=18$	Latifi and Jalali (2018)
Iran	TSP	57.4	–	$N=8$	
Iran	SSP	17.7	–	$N=5$	
Iran	DAP	19.2	–	$N=7$	
Iran	MAP	6.3	–	$N=3$	
Chile	TSP	143.5	18.9–288.4	$N=4$	Molina et al. (2009)
Chile	DAP	20.4	17.4–25.9	$N=4$	
Chile	MAP	18.8	11.9–22.0	$N=4$	Smidt et al. (2012)
Brazil	–	140.9	6.4–433	$N=39$	Lugon-Moulin et al. (2006)
Brazil	TSP	57.8			
Brazil	NPK	61.4			
Brazil	NPK	48.6			
Brazil	NPK	65.2			
Brazil	MAP	0.27			
Brazil	MAP	97.5			
China	DAP	4.46			
China	NPK	5.54			
China	NPK	9.56			
India	DAP	13.29			
Vietnam	DAP	3.0			
Vietnam	SSP	3.35			
Turkey	DAP	21.94			
Turkey	MAP	6.27			
Turkey	NPK	29.52			
Malawi	NPK	1.15			
Tanzania	NPK	1.04			

[a] MAP, monoammonium phosphate; DAP, diammonium phosphate; TSP, triple superphosphate; NPK, compound nitrogen, phosphorus and potassium fertilizer.

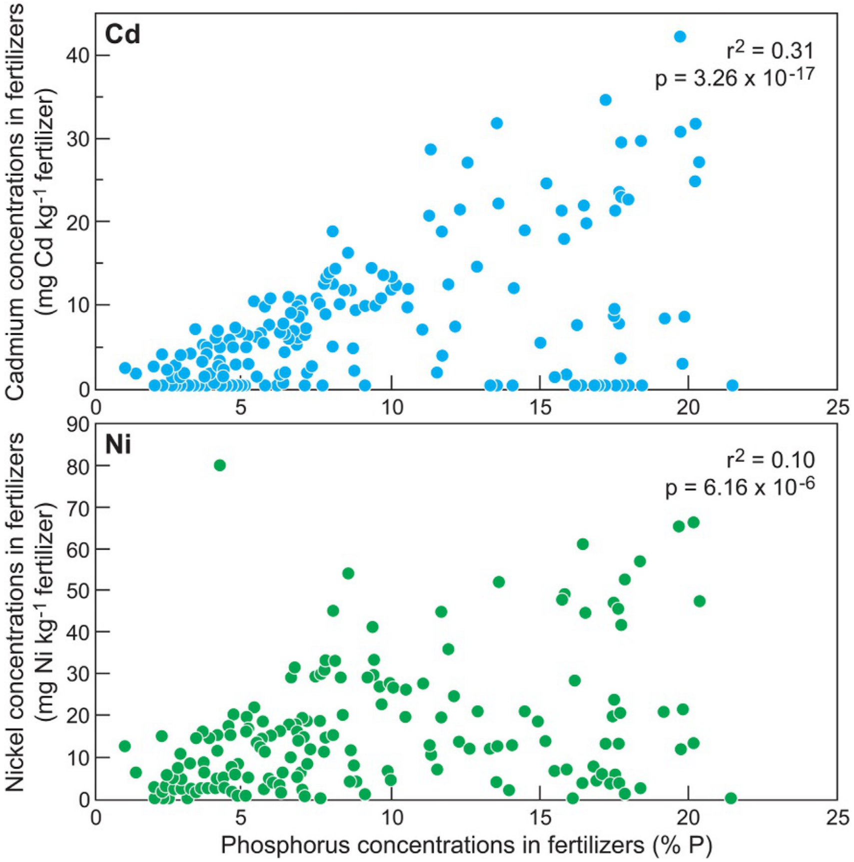

Fig. 4 The relationship between Cd concentration in phosphate fertilizers and the P weight percentage in the different mineral fertilizers. *From Nziguheba, G., Smolders, E., 2008. Inputs of trace elements in agricultural soils via phosphate fertilizers in European countries. Sci. Total Environ. 390, 53–57, with permission.*

generally low Cd concentrations in the P fertilizers used in China (Yu et al., 2018). This wide range of Cd concentrations in the final fertilizer reported in the literature is due to use of different phosphate rocks for fertilizer manufacture.

In order to limit the input of Cd in soils, several countries have introduced limits on Cd concentrations in phosphatic fertilizers. The EU Commission Regulation has only recently approved a limit of 137 mg Cd kg^{-1} P (60 mg Cd kg^{-1} P_2O_5) for fertilizers marketed in EU countries.[i] The application of the new regulation implies that currently 8% of the

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[i] https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32019R1009

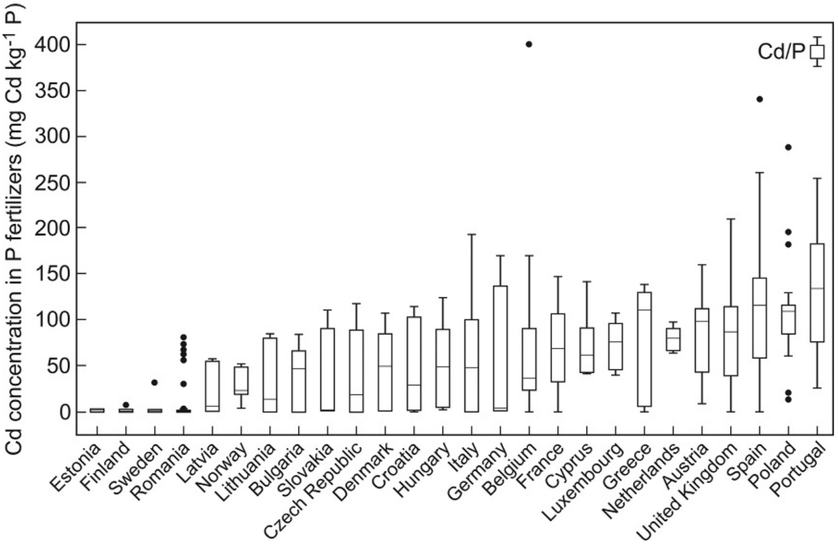

Fig. 5 Cadmium concentrations in mineral fertilizers (mg kg^{-1} P) according to country of origin ($n=403$); *Box plots and whiskers* indicate interquartile, *points* are outliers. The new EU limit of 2019 is 137 mg kg^{-1} P. *From Verbeeck, M., Salaets, P., Smolders, E. 2020. Trace element concentrations in mineral phosphate fertilizers used in Europe: a balanced survey. Sci. Total Environ. 712, https://doi.org/10.1016/j.scitotenv.2019.136419, with permission.*

fertilizers in the EU exceed the Cd limit (Verbeeck et al., 2020) and thus the removal of such fertilizers from the market would decrease the average Cd input in soils. The application of stricter Cd limits for phosphate fertilizers imply that phosphate rock with low Cd should be used or that decadmiation of phosphate rock or phosphoric acid needs to be considered when low Cd raw materials become limited. Decadmiation technologies have been investigated but not adopted at industrial scale as current methods are not cost-effective (de Boer et al., 2019).

The fertilizer application rate (kg P ha^{-1} yr^{-1}) logically also determines the input of Cd from fertilizers in soils. However, because addition of Cd in phosphate fertilizer at normal agronomic rates of P application is low relative to background Cd levels, major changes in Cd concentrations in soil will take many years to develop. Where P application rates are declining (in many developed countries), the time taken to detect changes in soil Cd concentrations will be longer. The consumption of fertilizer in European countries decreased sharply in 1990 and since then this trend has not changed (Schoumans et al., 2015). Consumption of mineral P fertilizer in Europe for agricultural use in 2016 was 3.8 Tg, about a 7% decrease from 2002;

whereas Asia is currently the world's largest consumer of phosphate fertilizers with nearly 30 Tg in 2016 (FAOSTAT, 2016). When the consumption of P is calculated on an arable land basis, the average annual consumption in European countries is 9.6 kg P ha^{-1} (22 kg P_2O_5 ha^{-1}) (Six and Smolders, 2014). Using the mean Cd concentration of 61.8 mg Cd kg^{-1} P, the average calculated annual input in the soil in the EU is currently 0.6 g Cd ha^{-1} yr^{-1}. This means that this input largely exceeds the input via atmospheric deposition (Table 2) but that both input values have decreased significantly from historical ones. The inputs of Cd from mineral fertilizers in China are less important than inputs from atmospheric deposition, because Cd concentrations in the domestic phosphate rock are below those used in Europe (Jiao et al., 2012; Luo et al., 2009). Phosphate rock from China comes mainly from sedimentary deposits with Cd contents <2 mg kg^{-1} (Roberts, 2014).

There are many reports of increasing Cd concentrations in soils from the historic use of phosphatic fertilizers. Increases in soil Cd concentrations associated with long-term P fertilization have been observed in studies in the United States (Mulla et al., 1980), Norway (Baerug and Singh, 1990), Denmark (Christensen and Tjell, 1991; Dam Kofoed and Sondergard-Klausen, 1983), Finland (Mäkelä-Kurtto et al., 1991), Sweden (Andersson, 1977), Britain (Jones et al., 1987b; Nicholson et al., 1994), Canada (François et al., 2009; Grant et al., 2014; Lambert et al., 2007), Australia (Williams and David, 1976), New Zealand (Gray et al., 1999; Loganathan et al., 1995, 2003; Roberts et al., 1994), and Ireland (McGrath and Tunney, 2010). In contrast, in field studies in Sweden, the effect of Cd added in P fertilizers over a 15-year period was minor compared to variation caused by uncontrolled factors (Andersson and Hahlin, 1981). In field studies in the United States, long-term application of fertilizers containing less than 5 mg kg^{-1} did not measurably increase soil Cd concentration (Mortvedt, 1987). In Britain, there was no measurable accumulation of Cd in soil after 27 years of phosphate fertilizer application (Richards et al., 1998). Similarly, neither total nor available soil Cd in soils was measurably affected by application of P fertilizer containing an estimated 46 mg Cd kg^{-1} P over a 70-year period in a long-term field study in Norway (Jeng and Singh, 1995). In trials across western Canada, increases in DTPA-extractable Cd over 9 years of application were minor at recommended rates of P fertilization or with fertilizers containing low Cd concentrations (Grant et al., 2014). Clearly, increases in soil Cd concentrations will be most evident where higher Cd fertilizers are used, over longer time periods and on soils where leaching or crop removal is low.

Inputs of Cd in fertilizers have likewise been reflected in increased concentrations of Cd in crops grown on those soils. In many long-term field studies, plant Cd concentrations were shown to increase with increases in soil Cd concentrations from P fertilizer application (Jones et al., 1987a; Jones and Johnston, 1989; Kashem and Singh, 2002; Mulla et al., 1980; Williams and David, 1976) indicating that Cd accumulation in soil increased concentrations of phytoavailable Cd in soil. For example, in long-term field studies, seed Cd concentration increased with increasing P applications when the fertilizer contained from 70 to 150 mg Cd kg^{-1} (Andersson and Siman, 1991). Cadmium concentrations of canola and wheat increased due to accumulation of Cd from P fertilization in a sandy soil, with a high correlation between soil test Cd (extracted with 0.005 M $CaNO_3$) and plant Cd concentrations (Brennan and Bolland, 2004). Repeated applications of high rates of P fertilizer containing high concentrations of Cd increased Cd concentration in flaxseed and durum wheat (Grant et al., 2013, 2014) (Fig. 6).

In other studies, the Cd availability and concentration in crops was not increased despite an increase in soil Cd concentration from P application. In long-term field experiments in Norway, soil Cd concentration was higher but crop Cd concentration was lower in long-term cultivated soils than in

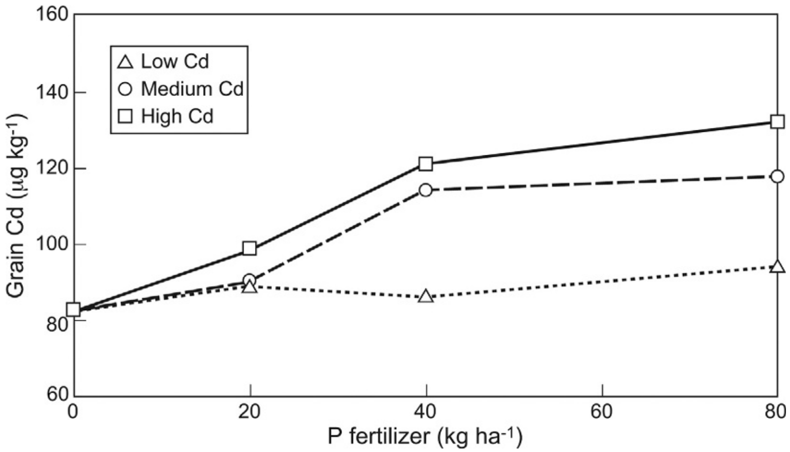

Fig. 6 Effect of 7 years of application of monoammonium phosphate fertilizer with varying Cd concentration on Cd concentration in durum wheat grain, averaged over six locations on the Canadian prairies. Low, medium and high Cd fertilizers contained 0.38, 71, and 211 mg Cd kg^{-1}, respectively. *From Grant, C., Flaten, D., Tenuta, M., Malhi, S., Akinremi, W., 2013. The effect of rate and Cd concentration of repeated phosphate fertilizer applications on seed Cd concentration varies with crop type and environment. Plant Soil 372, 221–233, with permission.*

newly cultivated fields with no anthropogenic Cd addition (Andersson and Hahlin, 1981; Baerug and Singh, 1990). The pH in the newly cultivated soils was lower than that in the long-term cultivated soils, possibly leading to higher Cd availability. Similarly, at Rothamsted, England, the Cd concentration of grasses grown on plots that had received P fertilizer since 1859 were similar to those grown on unfertilized plots if pH had been raised by liming while in the unlimed plots, the fertilized grasses had a higher Cd concentration than the unfertilized grasses (Nicholson et al., 1994). In studies on soils across the Canadian prairies, Cd added in P fertilizer increased crop Cd concentration to a greater extent in low pH, coarse-textured soils than on high pH, clay loam soils (Grant et al., 2013, 2014).

Since changes in soil Cd concentrations from P fertilization will be related to the balance between Cd input and Cd removal over time, increases in soil Cd concentration related to P fertilization can be moderated either by reducing the concentration of Cd present in the fertilizer or reducing total fertilizer applications. Selection of proper rate of application based on an effective soil P test, combined with use of source, placing and timing combinations will reduce the amount of P applications needed to optimize crop yield and hence reduce the input of Cd from fertilizer applications (Grant and Flaten, 2019).

2.2.3 Biosolids (sewage sludge)

The term biosolids refers to the solid residue that remains after treatment of municipal sewage sludge, which can be safely managed to benefit from its nutrient content (USEPA, 1993). Biosolids are a valuable source of macro- and micronutrients and organic matter and therefore are applied to agricultural soils to improve fertility and physicochemical properties. Land application is also the cheapest way for biosolids disposal. Biosolids typically contain 2–8% N, 1.5–3% P, 0.1–0.6% K, 0.6–1.3% S and 1–4% Ca (Cogger et al., 2006).

Unfortunately, biosolids also contain trace contaminants including Cd that are of concern as they can accumulate in the soil after continuous land application, potentially posing risks to human health and the environment. Typical concentrations of Cd in biosolids reported in the literature range from 1 to 70 mg Cd kg^{-1} dry weight (Table 4) (Haynes et al., 2009).

Biosolid Cd concentrations have decreased over the last decades and this is due to the application of strict environmental regulations (Oliver et al., 2005). For example, in USA the average Cd concentration in biosolids produced from wastewater treatment plants decreased from 110 to 6 mg

Table 4 Cadmium concentration in biosolids (sewage sludge) mg kg^{-1} (dry weight basis) reported in the literature.

Country	Mean	Min–Max	References
America			
Brazil	8.2		Sampaio et al. (2015)
Canada	0.8[a]		Hosseini Koupaie and Eskicioglu (2015)
USA	5.2		Kim et al. (2010)
Asia			
China	3.0	0.05–16.8	Luo et al. (2009)
Europe			
Greece	5	2–8	Samaras et al. (2008)
EU	2.0[b]	0.4–3.8	Nicholson et al. (2005)
Oceania			
Australia	0.9	0.7–1.4	Nash et al. (2011)

[a] Average of historical (2006–2013) Cd concentrations measured in Westside Regional Municipal Wastewater Treatment Plant.
[b] Weighted mean concentration based on values reported by the EU countries (Nicholson et al., 2005).

Cd kg^{-1} between 1976 and 1996 (Chen et al., 2010). In Sweden, over the period 1970–2010, Cd concentrations decreased in biosolids from 10 to 1 mg Cd kg^{-1} (Kirchmann et al., 2017). Similarly, Cd wastewater concentrations have decreased threefold in China from 1999 to 2005 (Luo et al., 2009).

As with fertilizers, the extent of Cd accumulation in the soil depends on the total concentration of Cd present in the biosolids and application rate. In general, biosolids are applied based on N or P crop requirements and regulations for application are based on maximum concentrations of the contaminants in the biosolids and cumulative loading limits of the contaminants added to the soil (Haynes et al., 2009). For EU countries the limit for Cd concentration in sludge for use in agriculture[j] is 20–40 mg Cd kg^{-1} dry matter and the maximal annual load is 0.15 kg Cd ha^{-1} yr^{-1}. Several EU countries have adopted even stricter limits compared to the Directive, i.e. Denmark, Finland, Netherlands, with values <2 mg Cd kg^{-1} dry matter. In Australia, Cd limits for biosolids use depend on intended land use

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[j] https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:31986L0278

(agriculture, forestry, rehabilitation, etc.) with agricultural use limiting biosolid Cd concentrations to $<1\,\text{mg}\,\text{kg}^{-1}$ in some States (SA-EPA, 1997; Victoria, 2004a,b; WA DEC, 2002). The US-EPA Regulation 503[k] based on risk assessment has much higher thresholds than the EU Directive, with a Cd concentration limit in biosolids of $39\,\text{mg}\,\text{kg}^{-1}$ dry weight basis and an annual pollutant load of $1.9\,\text{kg Cd}\,\text{ha}^{-1}\,\text{yr}^{-1}$.

Recently, Six and Smolders (2014) estimated average input of Cd from biosolids in European soils, noteworthy is that these estimated fluxes are based on total EU-wide use divided by the total agricultural area. Such estimates are well below the input values in soils where sludge is applied since the biosolids are only applied in limited areas. That average Cd input is $0.05\,\text{g Cd}\,\text{ha}^{-1}\,\text{yr}^{-1}$, which was calculated assuming the average Cd concentration in biosolids in Europe was $1.8\,\text{mg Cd}\,\text{kg}^{-1}$ and a sludge application rate of $26\,\text{kg}\,\text{ha}^{-1}$. This input represents only 4% of the total Cd input for agricultural soils. The study by Luo et al. (2009) estimated that the total input of Cd from biosolids in Chinese soils was only 0.1% of the total input. This very small input was calculated because land application of sludge in China is very low (<10%) according to the authors.

On soils where biosolids are applied, logically much larger Cd inputs are obtained. For example, for England and Wales soils, Nicholson et al. (2003) estimated $19\,\text{g Cd}\,\text{ha}^{-1}\,\text{yr}^{-1}$ as the Cd input where biosolids are applied. This calculation was based on an application rate of $250\,\text{kg N}\,\text{ha}^{-1}\,\text{yr}^{-1}$ and a concentration of Cd in the biosolids of $3.4\,\text{mg}\,\text{kg}^{-1}$ dry solids.

2.2.4 Lime/gypsums

Gypsum ($CaSO_4 \cdot 2H_2O$) is applied to agricultural soils as a source of nutrients (Ca and S) and as a soil conditioner for amelioration of subsoil aluminum toxicity or for reclamation of sodic soils (Chen and Wick, 2011). Gypsum used for this purpose is obtained either from mining natural deposits or as by-product of industrial processes, i.e. phosphogypsum and desulfogypsum. Mined gypsum materials do not generally contain trace elements at levels of concern in terms of soil contamination. However, that is not the case for gypsum derived from industrial by-products. The Cd concentrations in phosphogypsum are notably lower than in phosphate fertilizers, however the applied doses of the former are much higher than those

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[k] https://www.govinfo.gov/content/pkg/CFR-2018-title40-vol32/xml/CFR-2018-title40-vol32-part503.xml

of the latter. Hence, phosphogypsum might considerably enrich soil with Cd where it is applied and may even outweigh inputs from P fertilizers.

Phosphogypsum, a waste by-product from wet-acid production of phosphoric acid, contains variable levels of metal impurities (Cd, Zn, barium (Ba)) and radionuclides (mainly uranium (U), thorium (Th) and radon (Ra)) depending on the composition of the phosphate rock and efficiency of the wet-process used (Rutherford et al., 1994). Some of the Cd in the phosphate rock transfers to the phosphogypsum by-product but the majority transfers to the phosphoric acid (Mortvedt, 1996). Other studies calculated 12% of Cd transfer from the phosphate rock to phosphogypsum (Pérez-López et al., 2010). Higher concentrations of Cd in phosphogypsum than in the raw material have been also reported, an enrichment due to impurities present in the sulfuric acid used during fertilizer processing (Rentería-Villalobos et al., 2010). In general, the concentration of Cd in phosphogypsum can range from 0.8 to 40 mg Cd kg^{-1} (IAEA, 2013).

In 2013, the estimated worldwide production of phosphogypsum was in the order of 160 million Mg and expecting to increase to nearly 250 million Mg in the next decade (IAEA, 2013). Due to the presence of various contaminants, only 15% of the total phosphogypsum produced is reused, mainly in agriculture, as a soil improver and in building materials (Rashad, 2017). Dumping phosphogypsum to the ocean has been prohibited in various countries so the vast majority is just stockpiled on land which is a serious environmental problem.

In the Cerrado region of Brazil, phosphogypsum has been used as a soil amendment for many years to neutralize subsoil acidity. The criteria to recommend its application is based on % aluminum (Al) saturation and/or exchangeable Ca content of the soil and rates are calculated based on the clay content of the subsoil (Caires and Guimarães, 2018). Because of the presence of toxic elements in this by-product material the environmental aspects of its utilization are now being considered. Studies that analyzed the total metal concentration in Brazilian phosphogypsum from igneous phosphate rock have reported values <1.5 mg Cd kg^{-1} (Mazzilli et al., 2012; Nisti et al., 2015; Saueia et al., 2013), which are lower than the maximum Cd concentration (8 mg kg^{-1}) acceptable for soil conditioners as established by Brazilian regulations (Saueia et al., 2013). It has been considered that such Cd concentrations in phosphogypsum are safe for its utilization, nonetheless the long-term accumulation of Cd in soils should be assessed.

In Huelva, Spain a large area (40,000 ha) of saline sodic soils has been reclaimed for agricultural purposes by the application of phosphogypsum at rates of 20–25 $Mg\,ha^{-1}$ (Abril et al., 2008). The reclamation process started in 1978 and halted in 2001 due to environmental concerns. The Spanish phosphate fertilizer industry in the region mostly processes phosphate rock from Morocco and Senegal which are known for their high Cd concentrations. A study was conducted to evaluate the long-term effect of phosphogypsum application on the enrichment of Cd in reclaimed marsh soils of Huelva and its transfer to tomato (*Lycopersicum esculentum* L.) plants (Abril et al., 2008). Cadmium concentrations in tomatoes grown in such soils were all below maximum allowable concentrations (50 $\mu g\,kg^{-1}$) for consumption but about one order of magnitude higher than those found in tomatoes of other origin in Spain. The total calculated Cd input was 420 g $Cd\,ha^{-1}$ in the total of six applications in the period from 1978 to 2001.

Liming materials such as calcium carbonate ($CaCO_3$), calcium hydroxide ($Ca(OH)_2$), calcium oxide (CaO) and magnesium oxide (MgO) are used in agricultural soils to neutralize soil acidity and correct soil pH. Like gypsum, lime is applied at high rates, i.e. 1–10 $Mg\,ha^{-1}$ and needs recurrent applications. Lime is also a source of Cd and levels can be elevated particularly if the lime has been recovered as a by-product during Zn and Pb ore refinement (Chaney, 2012). For example, Davies et al. (1993) reported Cd concentrations of 3.4 and 38 mg $Cd\,kg^{-1}$ in limestone material collected from mining areas, while the Cd concentration in normal agricultural limestone was $<0.05\,mg\,kg^{-1}$. Recent published information on metal concentrations in liming materials is scarce which hinders a better estimation of Cd input in soils from this source. A study that analyzed 23 agricultural limes collected in different Brazilian states indicated that the Cd levels in all the materials were $<0.1\,mg\,kg^{-1}$ (Gabe and Rodella, 1999). Kabata-Pendias (2010) indicated concentrations of Cd in agricultural limestone in the range 0.04–0.1 $mg\,kg^{-1}$. For European soils Six and Smolders (2014) estimated the application of lime product with 0.35 mg $Cd\,kg^{-1}$ CaO (average Cd concentration determined in Swedish lime) at 250 kg CaO ha^{-1} would add a Cd input of 0.09 g $Cd\,ha^{-1}\,yr^{-1}$, i.e. clearly lower inputs than from atmospheric deposition or fertilizers.

2.2.5 Manures

The application of animal manures to soil is a traditional agricultural practice for recycling nutrients and organic matter in agricultural soils. The majority of Cd in manure is mainly derived from the animal feed, which feed can be locally produced or can be imported. In the former case, manure application is not a net source at the farm scale but only recycles Cd that was previously taken up by crops. Logically, when the feed is mainly imported or when the animal food is supplemented with minerals containing traces of Cd, the manure Cd can be a vector of net enrichment to agricultural soils. For Europe, the Cd inputs from manure at a European level were estimated by Six and Smolders (2014) and these authors considered only Cd derived from animal feed that was imported into the continent. Based on this data a net Cd input of about 0.006–0.014 g Cd ha^{-1} yr^{-1} was estimated in Europe in 2010, these fluxes are similar to those of lime and are minor compared to the natural (geogenic) stock in soil.

Table 5 shows the concentration of Cd in different types of animal manures from surveys conducted in different countries. The Cd concentrations in manure in China are remarkably higher than in EU and deserve attention. The inputs of Cd from manures at field scale can be calculated based on the applied manure rate to supply N. For example, Wang et al. (2013) estimated a Cd input of 10 g ha^{-1} in a soil that received pig manure applied at a rate of 250 kg N ha^{-1} yr^{-1} in China. This input of Cd is sevenfold higher than the value reported by Nicholson et al. (2003) for pig manure applied in UK at the same rate, mainly because the Cd concentrations in the manures from China were also ten times higher. Along the same lines, Luo et al. (2009) concluded that livestock manures are an important source of Cd in Chinese agricultural soils accounting for about 55% of total Cd inputs. This high Cd input was explained by the high Cd concentrations in the manures due to an excessive use of additives in the feed, these additives are discussed below under veterinary pharmaceuticals in Section 2.2.7. Wang et al. (2013) calculated that Cd concentration increased by 63% and 196% in pig and poultry manures, respectively, between 1990 and 2008 due to much higher use of feed supplements after 2002 by the development of intensive animal production systems. The most recent data of Cd concentrations in manure of China are less alarming, showing that the mean and median Cd concentrations of >200 samples collected in 2014 are 0.67 and 0.14 mg Cd kg^{-1}, i.e. within the range of values found in Europe (Yang et al., 2017).

2.2.6 Industrial wastes

Application of industrial wastes to agricultural land has been considered only in the case that the material has a nutrient content or soil conditioning effect that confers any agricultural benefit (Miller et al., 2000). Some of these industrial waste categories include waste from food and drink preparation,

Table 5 Typical Cd concentrations (mg kg^{-1} dry weight basis) in different types of manures.

Country/ Region	Manure type	Mean (mg kg^{-1})	Min–Max	References
Canada	Dairy	0.17		Sheppard and Sanipelli (2012)
	Pig	0.32		
	Poultry layer	0.32		
	Poultry broiler	0.19		
Asia				
China	Dairy	0.92	0.10–5.21	Wang et al. (2013)
	Pig	1.30	n.d.–15.30	
	Poultry	1.48	0.1–14.24	
China	Cattle	0.73	n.d.–10.49	Zhang et al. (2012)
	Pig	8.38	n.d.–111.69	
	Poultry	4.05	n.d.–37.99	
China	Cattle	3.4		Luo et al. (2009)
	Pig	4.8		
	Poultry	3.4		
	Cattle manure	3.4		
	Composted manure	0.67	0.07–8.70	Yang et al. (2017)
Europe				
Austria	Cattle manure	0.54	0.13–1.0	Leclerc and Laurent (2017)[a]
	Pig manure	0.49	0.11–1.28	
	Poultry manure	0.35	0.15–0.89	
Germany	Cattle manure	0.33	0.26–0.50	
	Pig manure	0.38	0.28–0.48	
	Poultry manure	0.26	0.20–0.50	
Sweden	Cattle manure	0.16	0.08–0.36	
	Pig manure	0.31	0.14–0.69	
United Kingdom	Cattle manure	0.38	0.10–0.53	
	Pig manure	0.37	0.19–0.53	
	Poultry manure	0.67	0.20–1.16	

[a] Data are a compilation from the data collected in the AROMIS project 2005 (Leclerc and Laurent, 2017).

abattoirs, paper waste sludge, textile waste, waste from leather and tannery industries, slag from the steel industry, and waste from organic chemical and pharmaceutical companies.

Paper mill sludge generally has metal concentrations that do not represent a limiting factor for its application to soil. Data from the European survey on wastes conducted in 2001 indicate the average application rate of this material can vary from 15 to 30 $\mathrm{Mg\,ha^{-1}}$ (Gendebien et al., 2001). In Canada, application rates vary by province, for instance application of residues high in metals is limited to $<22\ \mathrm{Mg\,ha^{-1}\ 5\,yr^{-1}}$. Gagnon et al. (2010) reported that application rates exceeding 60 Mg (wet) $\mathrm{ha^{-1}\ yr^{-1}}$ can cause a significant accumulation of Cd in the soil (Table 6). Tannery sludge from industry using vegetable tannins is acceptable for land application. Tannery sludge from processes using mineral tannins are not allowed due to the elevated concentrations of chromium. Data from the EU survey reported that the application rate can vary from 50 to $80\,\mathrm{m^3\ ha^{-1}}$ (Gendebien et al., 2001).

Table 6 Cadmium concentrations ($\mathrm{mg\,kg^{-1}}$ dry weight) in different industrial wastes.

Country or Region	Industrial wastes	Mean	Min–Max	References
EU	Food and drink industry sludge	0.8	0.01–10	Gendebien et al. (2001)
Portugal	Agro industrial sludge (winery production)	4.6		Alvarenga et al. (2015)
EU	Mixed pulp and paper sludge	1	0–4	Gendebien et al. (2001)
Canada	Paper mill biosolids	4.7		Gagnon et al. (2010)
Portugal	Pulp mill primary sludge	1.4		Ribeiro et al. (2010)
Portugal	Pulp and paper mill wastes	3.5		Alvarenga et al. (2015)
Malaysia	Paper mill sludge	2.34	1.3–4.09	Abdullah et al. (2015)
Brazil	Tannery sludge compost	2.87		Santos et al. (2011)
EU	Tannery sludge	0.17	0.15–0.7	Gendebien et al. (2001)
Portugal	Slaughterhouse sludge	3.8		Alvarenga et al. (2015)
EU	Textile waste	0.5	0.15–1.2	Gendebien et al. (2001)

Wood ash, the by-product of wood incineration for energy generation, is increasingly produced. That ash can be used as a liming material for acid soils. The chemical composition of wood ash is highly variable and depending on the source of wood it can contain a range of metal contaminants including Cd (Pasanen et al., 2001; Saarela et al., 2005). Pasanen et al. (2001) reported Cd concentrations from <0.3 to 60 mg Cd kg^{-1} dry weight in Finnish wood ash, according to the Plant Production Inspection Centre of ash for use in agriculture. Wood ash is used in forests as fertilizer and to counteract acidification processes. In Finland, wood ash is applied to forest soils and the rates vary between 2 and 16 Mg ha^{-1}. Pasanen et al. (2001) calculated an input of Cd of 50 g ha^{-1} by the application of an average amount of 5 Mg wood ash ha^{-1} containing 10 mg Cd kg^{-1} dry weight. The calculated Cd input from wood ash is higher than the Cd input from P fertilizers (0.6 g ha^{-1}) even if a one-time application over 50 years is considered.

2.2.7 Veterinary pharmaceuticals

The intensification of animal production systems had led to the increasing use of additives in animal feeds that are often enriched with trace metals like Cu, Zn, manganese (Mn) and arsenic (As) for optimal animal growth and for their antimicrobial properties (Qian et al., 2018). For example, Zn is added in large doses to pig feed to prevent diarrhea even without a veterinary prescription and most of the ingested Zn is excreted in the faeces (Nicholson et al., 1999). Cadmium is a contaminant generally present in Zn compounds and so it is a plausible reason for its presence in high levels in manures, particularly in pig manure in China. Wang et al. (2014) reported Cd concentrations in pig feed ranged between 1.0 and 165 mg kg^{-1}. However, other studies indicate values from non-detectable up to 27.6 mg kg^{-1} (Li et al., 2010). The concentrations of Cd in manure reported in the study of Wang et al. (2014) show a right-tailed distribution suggesting that a smaller fraction of the feeds are highly contaminated with Cd, suggesting a need for more control of the quality of animal feed in China.

3. Chemistry of cadmium in farm inputs and in soils

3.1 Speciation

3.1.1 Solid-phase speciation in soils and farm inputs

As noted in the Introduction, Cd is present in nature predominantly as the Cd^{2+} ion and has a Pauling radius of 97 pm, similar to that of Ca (109 pm). This, along with its preference for sixfold coordination means that Cd often substitutes for Ca in minerals (Traina, 1997). Cadmium rarely occurs as a mineral ore alone and usually co-occurs as the sulfidic minerals greenockite and hawleyite (both CdS) in ores with ZnS or galena (PbS). Cadmium can also occur naturally in the discrete minerals monteponite (CdO) and otavite ($CdCO_3$).

In phosphate rocks, the elevated concentrations of Cd in sedimentary phosphorites and carboniferous shales are due to substitution of Ca by Cd in the structure rather than formation of a discrete Cd phosphate phase (Jeanjean et al., 1994; Sery et al., 1996). During manufacturing, most of the Cd in the phosphate rock is solubilized and where phosphoric acid is produced, the Cd in the rock is transferred to the phosphoric acid—only small concentrations of Cd are found in phosphogypsum (David et al., 1978; Williams, 1977). Cadmium present in granular phosphatic fertilizers is quite water soluble—Williams and David (1973) showed that on addition to moist soil, granules of single superphosphate (SSP) lost all of their P in 8 days but 60% of the Cd (and Ca) was retained in the granule. They also showed that Cd in the water extracts was approximately proportional to Ca extracted, indicating that Cd was associated with Ca in both the phosphate and sulfate components of the SSP fertilizer. Mortvedt and Osborn (1982) examined the plant availability of Cd in triple superphosphate (TSP) and diammonium phosphate (DAP) and concluded that Cd in these fertilizers had a similar availability as the pure Cd compounds, cadmium dihydrogen phosphate $Cd(H_2PO_4)_2$ and cadmium diphosphate ($CdHPO_4$), analogs to the Ca minerals monocalcium phosphate ($Ca(H_2PO_4)_2$) and dicalcium phosphate ($CaHPO_4$). There have been few studies on Cd solid-phase speciation in other farm inputs such as animal manures and biosolids—likely because the low concentrations do not allow X-ray spectroscopic techniques to identify any discrete Cd phases, but also because the Cd is most likely present as adsorbed species on organic matter or clay minerals in these matrices.

Cadmium in soils is predominantly present as Cd sorbed to mineral and organic matter surfaces and solution concentrations are more likely to be controlled by adsorption reactions than by solubility products (discussed fully in Section 4). Discrete Cd minerals have rarely been unequivocally identified in soils or farm inputs, likely because concentrations of Cd in these matrices are usually well below the solubility products of the most likely Cd minerals that could form. Furthermore, X-ray diffraction methods have detection limits too high to determine low concentrations of Cd minerals. Only in very highly contaminated soils or soils spiked with Cd to high concentrations would discrete Cd minerals be expected. Modern synchrotron

X-ray spectroscopic methods are probably the best techniques for detecting the ionic binding environment of solid-phase Cd, but again highly contaminated soils have generally been used (Karlsson et al., 2005; Karna et al., 2016; Khaokaew et al., 2011, 2012). For example, Khaokaew et al. (2011) found that Cd in an alkaline highly contaminated paddy rice soil (soil Cd concentration of $142\,\mathrm{mg\,kg^{-1}}$) was present predominantly as $CdCO_3$, with minor amounts of CdS and Cd associated with organic matter.

Many studies have used extractants to infer solid-phase Cd speciation from Cd solubility, e.g. Cd released by reagents that reduce Fe^{3+} in soil is assumed to be Cd associated with Fe oxides. Often several extractants are used in a sequence to partition Cd into various forms (Tessier et al., 1979), termed fractionation here (Krishnamurti et al., 1997; Krishnamurti and Naidu, 2000; Ma and Rao, 1997; Taylor et al., 1995). Similar techniques have applied to Cd in sewage wastes (Yaman and Bakirdere, 2003). However, these fractionation schemes are rarely selective for discrete metal phases; fractions are operationally defined (Nirel and Morel, 1990) and rarely are the fractions related to biological availability (McLaughlin et al., 2000b).

3.1.2 Solution phase speciation in soils

Cadmium is a strong Lewis acid with the first hydrolysis constant of the hexa-aquo ion being 10.1, meaning that in most soils with a pH less than 9, dissociated Cd is predominantly present as the hexa-aquo Cd^{2+} ion (McLaughlin et al., 1996) (Eq. 1).

$$\mathrm{Cd(H_2O)}_{6\mathrm{aq}}^{2+} \Leftrightarrow \mathrm{Cd(H_2O)}_{5\mathrm{aq}}^{+}\mathrm{OH}_{\mathrm{aq}}^{+} + \mathrm{H}^{+} : \mathrm{p}K_1 = 10.1 \qquad (1)$$

Measurement of Cd speciation in soil solutions is not straightforward as the concentrations of Cd in most porewater from agricultural soils are very low—generally less than 10 nM ($\sim 1\,\mu\mathrm{g\,L^{-1}}$). Early work examined liquid chromatographic methods, competitive chelation or use of ion specific electrodes (Hirsch and Banin, 1990; Mahler et al., 1980; Tills and Alloway, 1983; Workman and Lindsay, 1990), but had to use highly polluted soils or spiked soils to attain concentrations of Cd that were detectable once speciated. Later, methods were developed using ion-exchange resins (Holm et al., 1995; Lorenz et al., 1997) and voltammetry (Berggren, 1990; Sauvé et al., 2000b). Prediction of Cd speciation in soil solutions using thermodynamic equilibrium models, e.g. GEOCHEM (Parker et al., 1995) or MINTEQ (Gustafsson, 2010) has also been undertaken and is much easier than measuring Cd speciation directly, but relies on assumptions of the binding of Cd with dissolved organic matter. Perhaps the most robust direct measurement technique is Donnan dialysis (Berggren, 1990; Fitch and Helmke, 1989; Nolan et al., 2003) but again the method is not simple and can suffer from poor detection limits for less contaminated soils (Nolan et al., 2003).

There is general agreement, using the above methods, that Cd is present predominantly as the free Cd^{2+} ion in soil solutions, but can also be present as a complex ion in solution with various inorganic and organic ligands. Chloride (Cl^-) sulfate ($SO_4{}^{2-}$), bicarbonate (HCO_3^-) and dissolved organic matter are the most important complexing anions in agricultural soils (Del Castilho et al., 1993; Hahne and Kroontje, 1973; Nolan et al., 2003). In saline soils, high concentrations of either Cl^- or $SO_4{}^{2-}$ mean that much of the Cd in soil solution will be complexed by these ions and hence mobility and plant availability are significantly increased (Doner, 1978; McLaughlin et al., 1997b; Smolders et al., 1998). The complexation of Cd by dissolved organic matter in soil solution is not strong compared to other ions such as Cu and Zn (Lorenz et al., 1997; Nolan et al., 2003). However, in soils with large amounts of dissolved organic matter, or in rhizosphere soil, complexation of Cd^{2+} by organic ligands may be significant (Hamon et al., 1995).

4. Reactions of cadmium with soils and cadmium transport

4.1 Adsorption and precipitation

The Cd^{2+} cation has an electronic configuration of Pd° with a completely filled d-shell ($4d^{10}$), i.e. Cd is not a transition metal. However, the electron cloud of this cation is polarizable and is considered as a class B metal in the Schwarzenbach classification of metals (A = hard as Ca^{2+}, C = soft as Cu^{2+}), therefore Cd^{2+} participates in covalent bonding with surfaces and is, furthermore, less soluble than harder cations. Class B cations such as Cd^{2+} form inner sphere complexes with high selectivity onto surfaces whereas harder cations may bind as outer sphere cations. Below we will illustrate that Cd^{2+} forms definitively stronger bonds with soil particulates or soil colloids than Ca^{2+}, however these bonds are not as strong as for transition metals such as Cu^{2+}.

As noted above, Cd concentrations in the solution phase of uncontaminated (total Cd about $0.2\,mg\ Cd\,kg^{-1}$), pH neutral soils are typically below $1\,\mu g\ Cd\,L^{-1}$.This means that only a very small fraction of total Cd is present in soil solution and that annual losses of Cd by leaching are generally negligible. As noted earlier, the precise binding mechanisms of Cd in soil are almost impossible to detect with current spectroscopic techniques at environmentally relevant concentrations. Therefore, solubility data or chemical extraction data are used to indirectly infer Cd binding mechanism. Christensen (1984b) suggested that adsorption, and not precipitation, controlled solution Cd in the environmentally relevant concentration range in soils (0.1–10 mg Cd kg^{-1} soil). Sorption of Cd is quasi linear with almost no intercept within the environmental concentration range (Fig. 7). The concentration of Cd in solution increases almost proportionally to Cd addition whereas precipitation reactions would infer constant solution concentrations with increasing Cd additions.

Precipitation is unlikely to control Cd solubility except at excessive Cd contamination and at pH values >7.0. For example, the solubility product (K_{sp}) of $CdCO_3$ ($K_{sp} = 10^{-12}$), the most insoluble possible form of Cd in aerobic soils, predicts that Cd precipitates in calcareous soil at pH 7.5 only when solution Cd concentrations are above 55 μg Cd^{2+} L^{-1}. Sorption and solution complexation reactions in pH neutral soil (Fig. 7) typically reduce Cd^{2+} at that pH to <10 μg L^{-1} for soils up to 10 mg Cd kg^{-1}. This means that soil Cd concentrations should exceed >100 mg Cd kg^{-1} for this precipitation reaction to occur, clearly beyond the range of agricultural soil Cd concentrations. Further empirical evidence of Cd adsorption revealed that: (a) soil texture has a weak effect on Cd adsorption (somewhat more adsorption on sandy loam than loamy sand); (b) adsorption strength at low Cd concentrations is markedly larger than at very high concentrations (indicating binding site heterogeneity); (c) pH has a marked effect on Cd adsorption; and (d) Ca is much less strongly held than Cd on soil surfaces—a 10-fold increase of solution Ca^{2+} decreases Cd^{2+} adsorption only by a factor of 2–3 (Christensen, 1984b; Degryse et al., 2009a).

Soil organic matter, oxyhydroxides of Al, Fe and Mn and clay minerals are the main Cd sorbents in soil. Numerous sorption data on these isolated soil constituents have been collected and are now embedded in geochemical speciation codes. Protons are the main competing cations for Cd^{2+} adsorption on organic matter or oxyhydroxides because Cd^{2+} binds to surface oxygen atoms of carboxylic or phenolic groups of humic substances or to surface hydroxyl groups on oxyhydroxides. A general adsorption equation reads:

$$\text{S-OH} + Cd^{2+} = \text{S-OCd}^{+} + H^{+} \tag{2}$$

in which S-OH is the surface hydroxyl group. This simplified equation already predicts that increasing H^{+} decrease adsorption drastically.

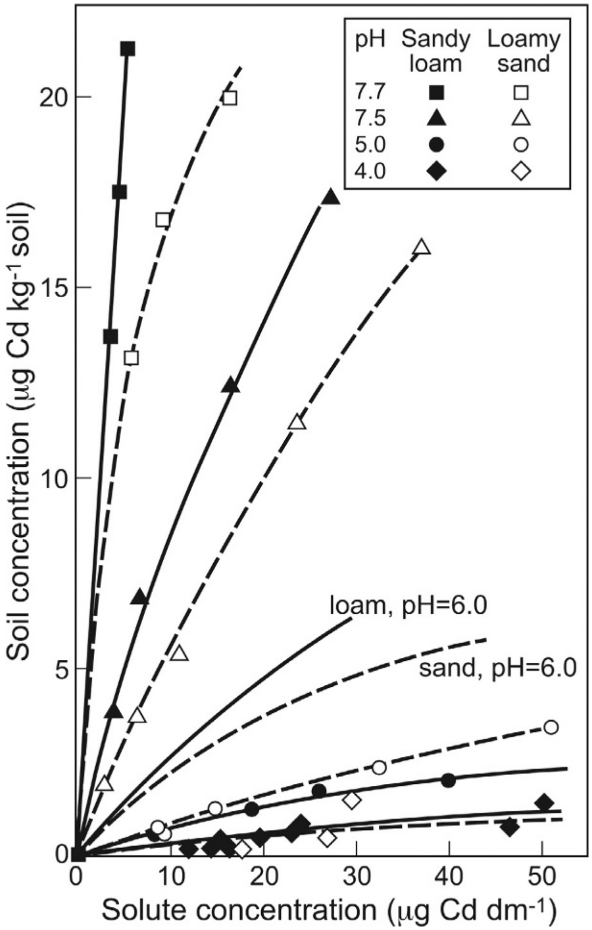

Fig. 7 Sorption isotherms of Cd determined in 10^{-3} M $CaCl_2$ for two soils at different pH values. The soil Cd concentrations (*Y*-axis) cover the range from background (<1 mg Cd kg^{-1}) to contaminated soils (1–10 mg Cd kg^{-1}). The typical soil solution Cd concentrations are also illustrated: <10 µg L^{-1} for soils above pH 6 and up to 50 µg L^{-1} in contaminated, acid soils. *From Christensen, T.H., 1984a. Cadmium soil sorption at low concentrations. II. Reversibility, effect of changes in solute composition, and effect of soil aging. Water Air Soil Pollut. 21, 115–125, with permission.*

The adsorption constants of Cd^{2+} to humic acids (the major sorptive phase of soil organic matter) and Fe-hydroxides are collated in geochemical databases such as WHAM VI (Tipping, 1994) or VMinteq 3.1 (Gustafsson, 2010) and these values show that Cd^{2+} binds orders of magnitude more selectively than Ca^{2+} (example: about 200-fold on humic acids at environmental conditions) but somewhat less than Zn^{2+} and orders of magnitude less than Cu^{2+}. Note, however, that Ca is present at 10^{-3} to 10^{-2} M whereas

Cd is present at 10^{-9}–10^{-7} M in soil solutions, i.e. Ca^{2+} is a competing cation for Cd^{2+} adsorption despite the pronounced Cd:Ca selectivity. The Cd^{2+}:Ca^{2+} selectivity for adsorption on clay minerals is typically less than fivefold at relevant conditions, therefore clay minerals are unlikely to be important adsorbents for Cd in most soils. Speciation modeling predicts that the majority of Cd is bound to solid-phase organic matter in soils with $pH < 6.5$ whereas Fe oxides become the most important adsorptive constituent at $pH > 6.5$. Exceptions to this rule exist: multivariate analysis of Cd bioavailability, not solubility, in 560 Ecuadorian samples revealed that increasing concentration of amorphous Mn oxides in soil statistically lower soil Cd bioavailability at constant pH, total soil Cd and %OC, suggesting an important role of Mn oxides as the Cd sorbent (Arguello et al., 2019). Indeed, Mn oxyhydroxides have a greater affinity to bind Cd than Al or Fe oxyhydroxides thus decreasing its bioavailability (Basta et al., 2005). Li et al. (2015) showed that selective removal of Mn oxides from a soil sample or from soil fractions had a larger effect on the Cd adsorption constant (affinity, not capacity) compared to selective removal of Fe oxides or organic matter.

As noted earlier in Section 3.1.2, Cd may form complexes in solution with soluble ligands that have reduced charge and mobilize Cd in soil. A well-known example of that is the formation of chlorocomplexes of Cd ($CdCl_n^{2-n}$) that increase Cd mobility by more than a factor 5 at 120 mM Cl^- compared to corresponding non-saline soils (Smolders et al., 1998). In non-saline soils, solution speciation data and modeling show that more than half of Cd is present as the free cation except at high pH where Cd-DOM complexes contribute to increased Cd mobility. Hence, dissolved organic matter (DOM) transport is not a major route by which Cd is mobilized from soils to groundwater or surface water.

There is a much greater database on Cd concentrations in soil extracts compared to the number of data available for Cd in soil solution (*in situ* data). Soil extracts with dilute salts (e.g. calcium chloride—$CaCl_2$ 0.01 M) may be used as a surrogates, but give somewhat lower concentrations due to dilution of Cd and changes in concentrations of ligands that affect Cd desorption. The *in situ* data, therefore, match soil extract-based adsorption models reasonably well.

Geochemical codes are increasingly used to calculate the mobility and speciation of trace metals, including Cd, in soils. The premise in these models is that of additivity of adsorption to various surfaces (Lofts and Tipping, 1998). This additivity means that different reactive surfaces are assumed to act independently, e.g. the total adsorbed Cd is the weighed sum of adsorption on humic substances, on Fe and Al oxyhydroxides and on clay minerals. These assemblage models, also termed multisurface models, are coded in different platforms (VMinteq 3.1, WHAM VI, PHREEQC). Recent developments in the geochemical models are correcting for the mere additivity assumptions and are accounting for the interaction of humic substances on Fe oxyhydroxides (Hiemstra et al., 2010). In addition, while reactions in the codes are typically among two components, now also the number of ternary surface complexes in the model has increased. A relevant example is to code the previously reported interaction of phosphate anions promoting Cd^{2+} sorption on ferrihydrite as a ternary complex in the CD-MUSIC model (Tiberg and Gustafsson, 2016). The alternative for these assemblage models is the use of statistical multivariate models, i.e. calibrating Cd solubility data in a range of soils to soil properties. Different empirical models have been evaluated and compared with the assemblage models (Degryse et al., 2009a; Groenenberg et al., 2012). The multisurface models have obviously a better conceptual basis and allow inferring Cd speciation in soils. For prediction, however, empirical models are more calibrated than the multisurface models. For the most recent EU-wide Cd mass balance studies, probably the largest collation of soil solution and soil extraction data was produced (440 different soils; Römkens and Smolders, 2018), predicting:

$$\log[\mathrm{Cd}_{\mathrm{solution}}] = 3.66 - 0.48 \cdot \mathrm{pH}_{\mathrm{CaCl2}} - 0.71 \cdot \log[\text{organic matter}] + 1.12 \cdot \log[\mathrm{Cd}_{\mathrm{soil}}] \qquad (3)$$

where $[\mathrm{Cd}_{\mathrm{solution}}]$ equals the measured Cd concentration in soil solution or in soil extract ($\mu g\,L^{-1}$), $\mathrm{pH}_{\mathrm{CaCl2}}$ corresponds to pH in $CaCl_2$, organic matter is the soil organic matter content ($\% = 1.7 \times \%$organic carbon) and $\mathrm{Cd}_{\mathrm{soil}}$ is the total soil Cd content in $mg\,kg^{-1}$ (here: *aqua regia* extractable Cd). The log notation is for base 10. This equation predicts that solution Cd decreases by a factor of 3 ($=10^{0.48}$) per unit pH increase, that doubling the soil organic matter content reduces solution Cd concentrations by a factor of 1.6 and the solution Cd increasing slightly more in proportion to total soil Cd concentration. Soil pH has the largest relative effect on solution Cd at a spatial scale.

Pure inorganic Cd salts are often used to identify dose–response data for risk assessments, but are not environmentally relevant sources of Cd pollution. Numerous claims have been made that Cd added by sewage biosolids or compost is less available than Cd salts because sludge particles also carry sorption sites (Basta et al., 2005). However, these claims have been challenged, at least for the initial years after biosolid application where even larger Cd solubility is found in biosolid-amended soils (McLaughlin et al., 2006). The larger solubility is attributed to higher concentrations of competing cations (e.g. trace metals) in biosolids. Eq. (3) also predicts that the effect of %OC on the partitioning coefficient (K_d) is indeed relatively weak: increasing soil organic carbon (C) from 2.0% to 2.5% by adding biosolids, composts or manures (requiring very large doses) lowers solubility only marginally. This means that increasing organic matter (OM) dose does not immobilize Cd strongly, unless in soil where the %OM is extremely low.

4.2 Slow reactions of cadmium with soil surfaces (aging)

Slow reactions and/or adsorption irreversibility have a large environmental consequence for Cd since these reactions may gradually lower Cd bioavailability and counteract the ongoing diffuse Cd emissions to soil. Laboratory studies have shown that Cd sorption in soil reaches equilibrium within hours and that adsorption is quasi fully reversible, even after >1 year aging after adsorption (Christensen, 1984b). This pronounced reversibility may be related to the relatively large ionic radius of Cd^{2+} (0.95 Å) that limits intraparticle diffusion in oxyhydroxides and that does not allow isomorphic substitutions in octahedral sites occupied by the smaller Al^{3+} or Fe^{3+} cations in minerals. However, long-term sorption data are always difficult to interpret since small changes in pH may already explain changes in mobility. Isotopic exchange has been subsequently used to more sensitively detect the reversibility in soils to which Cd has been added for longer periods. This method is based on the addition of a Cd^{2+} isotope (e.g. radioactive $^{109}Cd^{2+}$) that is equilibrated for a short period (1–7 days) after which the specific activity (SA) of Cd in solution ($^{109}Cd/Cd$ ratio) is measured. If this ratio is larger in solution than in the entire soil, then a fraction of the Cd in soil has not equilibrated with the freshly added ^{109}Cd, i.e. some (old) Cd is bound stronger than (freshly added) ^{109}Cd. The Cd in soil that is fully isotopically exchangeable is also termed "labile" Cd and is the fraction of total Cd that is equally mobile (available) as freshly added Cd. Hence, isotopic exchange allows detection of which fraction of Cd added over the long term has been immobilized through slow reactions and which fraction remains reversibly bound. In a study of 23 contrasting soils, amended with Cd and aged for >2 years, the labile Cd was >80% of added Cd at $pH < 6.5$ but was lower at higher pH; hence aging reactions are unlikely

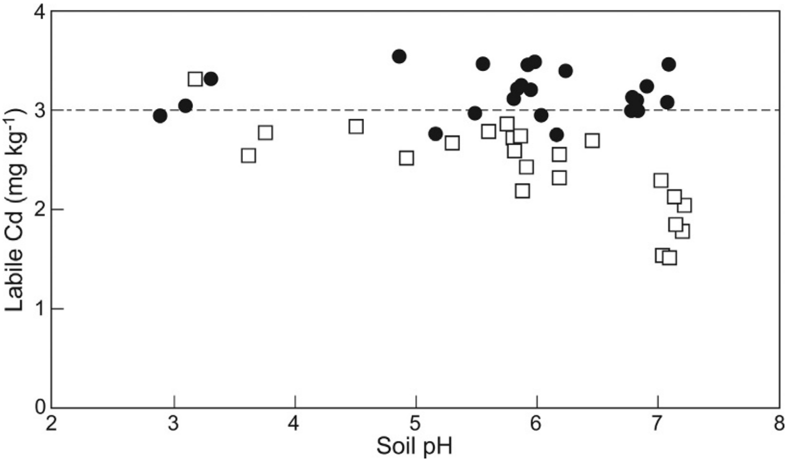

Fig. 8 Long-term reactions of Cds in soil: the concentration of radio-labile Cd after 11 (•) and 818 (□) days of incubation in 23 soils amended with 3 mg Cd kg^{-1} at day 0. Note that aging does not reduce Cd availability more than about 20% unless at pH > 6.5. *From Tye, A.M., Young, S.D., Crout, N.M.J., Zhang, H., Preston, S., Barbosa-Jefferson, V.L., Davison, W., McGrath, S.P., Paton, G.I., Kilham, K., Resende, L., 2003. Predicting the activity of Cd2+ and Zn2+ in soil pore water from the radio-labile metal fraction. Geochim. Cosmochim. Acta 67, 375–385, with permission.*

to be an environmentally relevant process that minimizes Cd bioavailability, except at high pH (Fig. 8) (Tye et al., 2003).

Similar conclusions apply to studies in which the SA of Cd was measured for the bioavailable pool, i.e. using the SA of Cd in spiked soils (Hamon et al., 1998; Smolders et al., 1999), both studies showing that Cd fixation in soils is detectable but is small and unlikely to be environmentally significant. Hence, it appears Cd added to soils does not become less available over time, as occurs for other metals (Hamon et al., 2007).

4.3 Redox reactions

Cadmium is present in soils at the Cd(II) oxidation state and does not change valence due to redox reactions in soils. However, soil pH increases when soils become waterlogged and this may explain immobilization of Cd when soils are submerged, i.e. in flooded rice culture. Maintaining soil under submerged conditions is a highly effective way to reduce Cd uptake by rice plants (Arao et al., 2009; Hu et al., 2013). Sulfides that form in strongly reduced soil may precipitate Cd^{2+} as CdS and render solubility well below 0.1 μg L^{-1} (Barrett and McBride, 2007). These sulfides are rarely present as pure sulfides and it is more likely that mixed Zn/Cd sulfides are formed (de Livera et al., 2011). Solid solution theory predicts a lower solubility for Cd substituted in ZnS than for pure CdS but this has not been observed (de Livera et al., 2011). In flooded rice systems, soils are drained a few weeks before maturity and this drainage causes oxidation and the release of S-bound Cd.

It has been hypothesized that CdS oxidizes more rapidly than pure ZnS, resulting in greater relative bioavailability, plant uptake, and translocation of Cd during the grain-filling period of rice growth. However, that hypothesis was not confirmed in oxidation experiments with environmentally relevant Cd-containing sulfide minerals (mixture of Fe, Zn and Cd), where the Cd release from sulfides was more limited than that of Fe or Zn (de Livera et al., 2011). These experiments were not performed in model solutions, but in soils and the authors speculated that Zn released by sulfide oxidation in soil might be retained more strongly than Cd on the new Fe(III) oxide surfaces formed, hence increasing the Cd:Zn concentration ratio in soil solution and increasing Cd acquisition by plants.

4.4 Leaching

As noted above, Cd is strongly bound in soil, so only minute fractions of it are present in soil solution and, hence, the removal by vertical leaching is small unless the soils are very acidic and low in organic matter. Despite this, the vertical leaching of Cd has become a focal point of attention and even controversy in the debate on the Cd limits in fertilizer in Europe that took place between about 1998 and 2018 (Sterckeman et al., 2018, 2019). The limits had been derived based on the average stand still (zero net accumulation) principle, not based on health risk assessment. The principle of zero net accumulation dictates that the mass balance of Cd should be zero, i.e. that the inputs from fertilizers and other sources should balance the output by removal with the crop and with leaching. The output by removal of crop is the product of the yield of the harvested crop and the Cd concentration in that crop. These data can be measured with high precision and accuracy. In contrast, the accurate estimate of the minute quantities of Cd that leaves soil by vertical leaching is difficult for technical reasons and, hence, the controversy regarding the assessment of the Cd limits is mainly about the methods to quantify Cd leaching from topsoils. Table 8 readily illustrates that the estimated leaching of Cd in European soils is about equal to that of the annual input minus crop offtake, i.e. the annual flux by leaching is the critical process that closes the Cd balance.

The annual loss by leaching is typically <0.1% of the total stock of Cd in the topsoil (Imseng et al., 2018), i.e. it is impossible to detect this flux from observed mass balances over even a few decades. Leaching also does not sufficiently change the isotope ratio of the naturally present stable isotopes to be useful to infer long-term leaching fluxes (Imseng et al., 2018). The most straightforward methods to determine Cd leaching are based on measurements of so-called flux concentrations, i.e. leachates that are continuously collected and that capture the entire annual flux of the leachates. This can be done with, for example, wick samplers that can be installed below the plow layer, thereby capturing the percolating water and maintain water unsaturated conditions at the sampling point. As far as we know, only two such datasets have been published (Degryse and Smolders, 2006; Filipović et al., 2016) Alternatively, suction cups are used for point estimates of pore water concentrations in the field; these data, combined with estimated annual drainage, yield estimated fluxes (Imseng et al., 2018) and references to this method in Six and Smolders (2014). Finally, modeling can be used to estimate the pore water concentration from soil properties and flux can be calculated knowing the estimated drainage. This last approach was used to estimate leaching at a larger scale in most of the mass balances by Six and Smolders (2014) (and references therein) and Römkens and Smolders (2018). The pore water Cd concentration models are, in turn, derived from surveys of such data and multivariate analysis to predict such concentrations from associated soil properties. In evaluating the models, it is instructive to recall the equation that the annual leaching flux of Cd (g Cd $\mathrm{ha}^{-1}\ \mathrm{yr}^{-1}$) is the product of the annual water drainage (D, defined in m water yr^{-1}) and the concentration in the pore water $(\mathrm{Cd})_{\mathrm{solution}}$, the latter in mg Cd L^{-1}.

$$\mathrm{Leaching} = 10,000\ \mathrm{D}\ (\mathrm{Cd})_{\mathrm{solution}} \tag{4}$$

Leaching is spatially variable because both D and $\mathrm{Cd}_{\mathrm{solution}}$ vary among soils and climates: D is large in wet areas and become small (or even negative: upward migration) in arid areas. The solution Cd depends on the local soil Cd concentration and increases with increasing acidity (and Cl^- salinity) and decreasing organic matter content. Leaching decreases as soil depth increases, that is because both D and (Cd) solution decrease, the former due to water uptake of deeper roots, the latter because soil total Cd concentrations in soil tend to decrease as depth increases. Hence, it is imperative to evaluate models with measurements when equal depths are compared. There are logically uncertainties to both D and $\mathrm{Cd}_{\mathrm{solution}}$ terms; both are derived from generic data or models and it is imperative to propagate the errors to identify the model uncertainties in the leaching to identify the errors in the steady state conditions (and hence the calculated Cd limits in fertilizers). None of these methods are free of errors; the wick samplers may undersample leaching fluxes as the wick may retain soil colloids. Porewater data may overestimate leaching when non-equilibrium occurs; desorption of Cd from soil may be slower than the water transport and preferential water flow may occur. Porewater data may also underestimate the Cd leaching when pore water colloids are filtered prior to analysis, thereby underestimating the colloidal transport of Cd.

In the model of Six and Smolders (2014), an average Cd leaching for the plow layer of European soils (0–25 cm) of 2.6 g Cd ha^{-1} yr^{-1} was estimated. That average value was considered relatively high compared to earlier estimates but was ascribed to a previously underestimated severity of soil acidity for European agricultural soils. The uncertainty of the leaching model has been emphasized in Six and Smolders (2014), but at that time validation with independent data of other estimation methods was deemed acceptable, as can be found in the discussion section of that paper. In 2018, the dataset for the porewater Cd data model was merged with other data from the University of Wageningen to obtain a larger dataset that encompasses more soils with low Cd concentrations and higher pH and a new model for estimating porewater Cd was derived that yielded about twofold lower Cd concentration and, hence, twofold lower Cd leaching fluxes.

Since the development of the models of 2014 (Six and Smolders, 2014) and 2018 (Römkens and Smolders, 2018), more field data of leaching were published and one dataset of 2006 had been overlooked (Table 7). These data show that leaching at field scale is generally <1 g Cd ha^{-1} yr^{-1}. The models used in the mass balances (Table 8) for Europe estimated an EU25 (surface area) mean Cd leaching of 1.1 g Cd ha^{-1} yr^{-1}. These models largely overestimate the corresponding field observations listed in Table 7, in some cases by up to two orders of magnitude, the largest overestimation being for the observations that showed the lowest leaching. This overestimation requires attention because the leaching term closes the mass balance estimates and determines the acceptable Cd emissions under steady state as described above.

The first dataset of leaching comes from suction cups with 0.2 μm filters, sampled at 50 cm depth during one hydrological year in 2014–2015 at three locations in Switzerland (Imseng et al., 2018). Cadmium leaching was calculated from the product of Cd concentration in these suction cups multiplied with the annual water drainage derived from soil physical calculations. At the site with the most acidic soil, Cd leaching was in the range of

Table 7 Recent estimates of Cd leaching under agricultural soils and its relationship to that estimated by the leaching models that were used in Europe for decision making on Cd limits in P fertilizers.

Dataset	Soil depth	Annual Cd leaching to deeper layers	Factor overestimated leaching (predicted/observed)	
		g ha^{-1} y^{-1}	Model I (Six and Smolders, 2014)	Model II (Römkens and Smolders, 2018)
Imseng et al. (2018)				
Three arable lands in Switzerland	50 cm	0.02–0.99	25–250	10–150
Filipović et al. (2016)				
Arable land in France amended with different organic fertilizer (three treatments)	45 cm	0.11–0.13	10–19	5–8
Bengtsson et al. (2006)				
Arable land of organic farms in Sweden (two sites)	0–20 cm	0.47–0.61	4–11	2–4

predicted values in the mass balance assessments (~1 g Cd ha^{-1} yr^{-1}, Table 8). However, when taking the actual soil composition at 50 cm depth, the model predicts a much 10–25 higher pore water Cd concentration than observed and this overestimation is even more pronounced for the pH neutral sites. In these pH neutral sites, the leaching was negligible (<0.1 g Cd ha^{-1} yr^{-1}) and leachate concentrations were in the ng Cd L^{-1} range (3–11 ng L^{-1}), close to the quantification limits of ICP-MS, whereas soil composition and the models predicted that it should be in the μg L^{-1} range. It might be questioned to what extent these dissolved (0.2 μm filtered) concentrations truly reflect the losses from soil; colloidal movement and/or erosion might become more dominant. This is indeed suggested when confronting the 1-year losses with the long-term losses; in the same study, long-term losses of Cd by weathering and leaching from the parent rock were estimated based on the Cd and titanium (considered immobile) concentrations in the soil profile, these data suggest that 25–79% of the Cd in the profile was removed by leaching from the top 50 cm during the about 13,700 years of soil development. In contrast, the very small

Table 8 Soil Cd mass balances (g Cd ha^{-1} yr^{-1}) considered in different studies.

	Europe				**China**	**Oceania**
Year and country	**1986–UK (Hutton and Symon, 1986)**	**1998–The Netherlands (Moolenaar and Lexmond, 1998)**	**2017–France (Sterckeman et al., 2019)**	**2017–EU-25 (Römkens and Smolders, 2018)**	**2008–China (Luo et al., 2009)**	**2013–Australia[a] (de Vries and McLaughlin, 2013)**
Inputs						
Atm. dep.	3.0	1.3	0.2	0.4	4.0	0.2
P fertilizers	4.4	2.5	1.4	0.6	0.9	1.2
Manure, sludge and compost	0.9	0.1	0.3	0.3	6.4	
Total input	*8.3*	*3.9*	*1.9*	*1.4*	*11.4*	*1.4*
Outputs						
Crop offtake		0.6	1.0	0.3	1.5	0.2
Leaching		1.6	0.5	1.1	n.d.	1.0
Total output		*2.2*	*1.6*	*1.4*	*1.5*	*1.2*
Net balance	*n.d.*	*+1.7*	*+0.3*	*+0.1*	*9.9*	*+0.2*
Balance (% change y^{-1})[b]		*+0.22*	*+0.04*	*+0.01*	*+2.5%*	*+0.05*

[a] Scenario of dryland cereals on sandy soils with mineral P fertilizer, no biosolids.

[b] Recalculated by authors here based on actual soil Cd concentration in the corresponding region and mean soil mass or plow layer.

Balances are selected that give regional or country averages, not site-specific balances that are affected by local conditions such as high biosolids (sewage sludge) loading or point pollution from stack emissions.

n.d. not determined or not considered in the study.

annual leaching losses, multiplied by that 13,700-year period, yields Cd losses of only 6–12%, illustrating that the "observed" 1 year leaching estimates with these pore waters are in conflict with the long-term losses by weathering.

The second dataset of leaching comes from wick samplers that had been installed at 45 cm depth in an agricultural soil where a field trial was performed on different organic fertilizer amendments (Cambier et al., 2014; Filipović et al., 2016). The leachates were monitored during six consecutive years between 2004 and 2010. The conclusion of the new but limited validation (Table 7) is that both models overestimate the Cd fluxes because of overestimates of porewater Cd concentration. The very low observed leachate Cd concentrations, near 10 ng Cd L^{-1} in pH neutral soils, appears at odds with the observed very long-term changes in soil Cd during pedogenesis (Imseng et al., 2018) and again suggest that colloidal movement of Cd is a yet underestimated contribution to Cd transport.

The last dataset obtained in Sweden in 2006 (Bengtsson et al., 2006) yields fluxes that are less overestimated by the models, the overestimation factors are 2–4 for the most conservative model. That study also gave leaching data for the deeper soil layers where similar overestimation factors apply.

Taken together, the models calibrated at a large scale overestimate the measured Cd leaching in the field. To some extent this may be due to the model being calibrated to surface soils where soil Cd is higher and pH is lower than in the subsurface. However, uncertainties exist in both the measurement and the models. The measurement uncertainties relate to potential exclusion of colloidal transport, i.e. leaching might be larger than observed. The model uncertainties relate to the variability of predictions: model uncertainty propagation in both the Six and Smolders (2014) or the more recent Römkens and Smolders (2018) study show that the leaching model uncertainty is too large to make meaningful claims about which Cd concentrations in fertilizers leads to zero net accumulation. More accurate estimates of Cd leaching are, therefore, core to the development of models to predict critical inputs of Cd to soils in agricultural inputs (fertilizers, manures, composts, biosolids) given the goal of many jurisdictions for zero net Cd accumulation in soil.

5. Accumulation of cadmium in soils

5.1 Data and models of cadmium accumulation in soil

The current (ambient) stock of Cd in soil is the result of the natural background and the enrichments from anthropogenic Cd emissions, these are mainly atmospheric deposition and applications of Cd-containing P fertilizers, biosolids and manures. The earliest record of such enrichments was probably in 1974 in Australia where soil Cd concentrations were found to increase with increasing rates of P fertilizers that had been applied for multiple years in experimental plots (Williams and David, 1973). Numerous collections of archived soil samples from experimental stations in Europe revealed that soil Cd concentrations had increased over time during the 19th and 20th centuries (Jones et al., 1987b; Juste and Tauzin, 1986; Tjell and Christensen, 1985). The factor increase in total soil Cd between the oldest archived soil sample and the most recent one, range from 1.3 to 2.6, logically depending on the length of the archived period, the magnitude of Cd inputs, etc. Archived wheat grain samples similarly revealed an increasing trend in Cd concentrations over the same period in some, but not all field trials (Andersson and Bingefors, 1985; Jones and Johnston, 1989). More recent studies, e.g. from New Zealand or Switzerland, have shown that the recent trends in soil Cd are more difficult to detect, likely as a result of reduced inputs from reduced atmospheric deposition (Bigalke et al., 2017) or reduced input of Cd in P fertilizers (Schipper et al., 2011).

The increase of soil Cd due to the emissions has led to several attempts to model the mass balance of Cd. This mass balance has been used to define critical loads or critical Cd concentrations in the amendments that do not lead to further increases in the soil Cd, i.e. leading to zero-net accumulation. In discussing these mass balance below, it is instructive to recall Section 2 where we showed that annual Cd additions to agricultural soils are much smaller than the stock of geogenic Cd in soil: annual additions are in the range 0.1–10 g Cd ha^{-1} yr^{-1} contrasting a geogenic stock in topsoil 300–1500 g Cd ha^{-1}. Hence, the soil Cd concentration changes are only detectable in long-term (>50 years) observations.

The mass balance is the net result of the summed annual additions minus summed losses and this is calculated for multiple years to predict trends in soil Cd concentrations. The inputs are the ones discussed in Section 2, outputs are leaching (Section 4.4) and removal of crop Cd, i.e. the product of the yield of the harvested crop and the Cd concentration in that crop. The outputs are modeled as a function of the current stock of Cd, i.e. they increase as the stock increases. The mass balances are typically made for the plowed (mixed) layer, about 25 cm for arable soils, about 10 cm for grasslands. Plant roots can take up Cd from much greater depths than 10 or 25 cm, this means that the selected depth for the mass balance may not reflect the trends in food chain exposure to Cd. If mass balances are made for deeper soil profiles, then the average concentration changes are logically less pronounced than corresponding balances for shallower depths. That selected soil depth is another critical parameter, even a controversial one, when zero net accumulation needs to be calculated; current low emissions may predict negative trends in soil Cd concentrations when a shallow soil depth is selected because leaching losses for the selected soil depth are larger when the soil depth is smaller. Hence, true zero net accumulation occurs at even lower emissions when the entire root zone, rather than part of it, is taken into account.

Several mass balances for soil Cd concentrations in Europe, China or Australia are compared in Table 8. The balances selected provide regional or country averages, not site-specific balances that are affected by local conditions such as high biosolids loading or point pollution from stack emissions. The balances logically depend on local emissions (fertilizer use, atmospheric deposition, etc.), on climatic and soil conditions (rainfall and soil pH) and on land use and the fate of the Cd taken up by crops (true offtake or recycled via manure). The mass balances have been made with increasing precision and the most recent one (Römkens and Smolders, 2018) calculates all these data of EU-25 with site-specific parameters, the results are implemented in a GIS to map the balances.

5.2 Cadmium mass balance in the EU and the controversy regarding fertilizer regulations for cadmium

The mass balances of Cd in Europe illustrate that the mean balance has evolved from a positive one (increasing concentrations) in earlier decades to almost zero net accumulation now. The balances made for the years <1990 in Europe were based on Cd input fluxes near 10 g $\mathrm{Cd\,ha^{-1}\,yr^{-1}}$, predicting a net Cd accumulation as confirmed by the archived soil data. The current average fluxes are now reduced to <2 g $\mathrm{Cd\,ha^{-1}\,yr^{-1}}$. These lower input values are close to annual output values. As discussed above, the annual Cd flux lost by leaching is the critical process that closes that balance, hence the uncertainty regarding leaching translates into uncertainty about the achievement of zero net accumulation. The uncertainty regarding the leaching models has been calculated by an error propagation approach in Europe (Römkens and Smolders, 2018). That analysis revealed that the leaching model uncertainty is too large to make meaningful claims about which Cd concentrations in fertilizers leads to zero net accumulation.

More exactly, it was stated that the "*predicted average change in soil Cd over the next 100 years was not statistically different from the current soil Cd content at* *any scenario of mean Cd concentrations in the fertilizers ranging between 20–60 mg Cd kg*$^{-1}$ *P*$_2$*O*$_5$" (Römkens and Smolders, 2018). Again, it must be emphasized that such a claim was made for an *average* scenario, with negative balances in some regions compensating for positive balances elsewhere and that there are regions in which the projected soil Cd accumulations or depletions are statistically significant, i.e. stated with low uncertainty. That uncertainty has been included as a response to the lengthy discussion and controversy about the Cd limits, the debate has been active for over 20 years in Europe, and there were various claims about overestimated leaching estimates or even biased views regarding the assessment.

5.3 Cadmium mass balances in China, Australia and South America

The Cd mass balance for China made in 2008 illustrates that this country had a positive soil Cd balance at that time (Luo et al., 2009). The input fluxes show that the major part relates to manure, not P fertilizers. Manure is not a net source of Cd at a country level if the Cd in manure is derived from Cd in animal feed that, in turn, is derived from soil in the same country. For that reason, European soil Cd mass balances at a large scale have largely ignored the manure Cd as a net input and only included the Cd imported with imported animal feed as the net source of Cd via manure. For China, it is yet unclear what this source is, some claim that that the Cd in manure is mainly derived from feed additives (Zn and Cu supplements) (Wu et al., 2012), i.e. a true net enrichments and we noted (Section 2.2.5 for a discussion) that the manure Cd concentration data are largely right skewed. A recent survey of metal concentrations in manures in China indicated that Cd concentrations were not excessive (Yang et al., 2017). Again, it is suggested that there is a need to further investigate this topic.

In Australia, accumulation of Cd in agricultural soils was well documented in the 1970s, indicating a positive mass balance historically due to the use of high-Cd fertilizers through use of phosphate rocks from Nauru and Christmas Island (McLaughlin et al., 1996; Williams and David, 1973). More recent modeling of Cd in four typical Australian agricultural systems has been undertaken based on detailed measurements of Cd in soils, soil solutions and produce and typical fertilizer use and quality data (de Vries and McLaughlin, 2013). In the period 1900–2000, soil Cd concentrations were predicted to increase on average between 0.21 mg kg^{-1} in dryland cereals, 0.42 mg kg^{-1} in intensive agriculture and 0.68 mg kg^{-1} in dairy production, which were within the range of measured increases in soils in those systems.

A dramatic reduction in Cd concentrations in fertilizers in the last 3 decades has dramatically slowed or halted Cd accumulation in soils, with current average Cd in P fertilizers of ~60 mg Cd kg^{-1} P. Critical fertilizer Cd concentrations were calculated not based on the philosophy of zero net accumulation, but on exceedance of soil, food or water quality limits for Cd, and these varied from <50 to >1000 mg Cd kg^{-1} P.

Research on Cd has intensified in South America since the new EU Cd regulations in cocoa products (see Section 1.3). High Cd concentrations in cacao beans in some South American countries are mainly explained by high geogenic soil Cd concentrations that, in turn, likely relate to the young age of the soils influenced by volcanic activities (Arguello et al., 2019). The question has been brought up in several studies to what extent the input of Cd from P fertilizers contributed to soil Cd in these systems. For example, a recent study identified the use of fertilizers as a management practice that significantly (*P*-value = 0.048) increased Cd concentration in cocoa powder produced from beans where the trees have been fertilized, i.e. about 3.5 mg Cd kg^{-1} dry matter with fertilization vs 1.8 mg Cd kg^{-1} without fertilization (Zug et al., 2019). These authors speculated about the role of P fertilizer and suggested that reduced fertilizer use may reduce bean Cd. However, the discussion in that paper noted that the effect of fertilizer was more related to N fertilizer, a low Cd-containing fertilizer, not P fertilizer, and higher N fertilizer use is known to enhance Cd bioavailability (Section 7.7.2.2). Along the same lines, soil Cd surveys conducted in South American cacao growing farms generally reported higher Cd concentrations in the topsoil (0–10 cm) than in deeper soil layers (Barraza et al., 2017; Chavez et al., 2015; Gramlich et al., 2017). These results have been suggested to relate to anthropogenic additions, where the application of phosphate fertilizers is one of the possible sources for Cd enrichment in cacao topsoils (Chavez et al., 2015; Gramlich et al., 2017). However, it is well known that natural biological cycling can bring Cd from subsoils to topsoils (Imseng et al., 2018; Reimann et al., 2019).

To date, it appears only the study conducted by Gramlich et al. (2017) has analyzed Cd concentrations in the fertilizers used in cacao-farm systems. The authors reported a high Cd concentration (235 mg Cd kg^{-1} P) in one of the commercial NPK fertilizers that were applied in conventional cacao farms. The dose of P fertilizers used in cacao crop range from 2.6 to 5.2 kg P ha^{-1} yr^{-1} (highest dose used in conventional monoculture systems). Using this abnormally high Cd concentration for P fertilizer, the calculated annual Cd input from such a source is 1.2 g Cd ha^{-1} yr^{-1}. In this study, total soil Cd concentrations measured in the topsoil (0–10 cm) and subsurface (10–25 cm) layers were 1.10 and 0.87 mg Cd kg^{-1}, respectively (Gramlich et al., 2017); which is equivalent to 2421 g Cd ha^{-1} in the topsoil. If the soil background Cd concentration is considered to be represented by the concentration in the 10–25 cm layer, then the difference in soil Cd concentration in the top layer between actual and background is equivalent to 506 g Cd ha^{-1}. At an annual dose of Cd via P fertilizer, it would take over 400 years of continuous fertilization with a high Cd source to enrich the topsoil layer (0–10 cm) to this level, which is unrealistic since fertilization is unlikely to have occurred for more than about 100 years. Chavez et al. (2015) measured total soil Cd concentrations to a greater depth (0–50 cm) in 19 farms and the mean difference in soil Cd between the 0–5 cm and the 30–50 cm layer was 0.65 mg Cd kg^{-1}, i.e. larger than the enrichment in the study of Gramlich et al. (2017). This means that it would take even longer for P fertilizer to explain that enrichment. Taken together, it is highly unlikely that the application of P fertilizers is an important Cd input in cacao farms of the region. Instead; the recycling of the geogenic Cd by leaf litter more likely explains the vertical Cd concentration gradient. In cacao farming systems plant material (leaves and twigs) from leaf shedding and from pruning practices are usually left in the field. The Cd concentrations in cacao leaves (mean 2.6 mg Cd kg^{-1} dry matter) are greater than those in soil (Arguello et al., 2019). Therefore, continuous cycling and accumulation of this material on the topsoil layer bring subsurface Cd to the surface.

6. Uptake and translocation of cadmium by plants

Cadmium is a non-essential and toxic metal for living organisms, with the exception of some marine diatoms, such as *Thalassiosira weissflogii*, which live in the Zn-poor environment of the surface ocean and, as a result, appear to have evolved a new type of Cd-dependent carbonic anhydrase instead of Zn (Lane and Morel, 2000; Xu et al., 2008). Because of this non-essentiality for most organisms, there are no biological reasons to evolve specific Cd uptake or transport mechanisms. However, Cd is a "super hitchhiker" for membrane transporters of a number of essential nutrients, such as Fe(II), Zn, Mn and Ca, due to similarities in their chemical and charge characteristics and imperfect selectivity of transporter proteins (Clemens, 2006; Clemens and Ma, 2016). Toxicity of Cd is partly caused by its competition with the transport of these essential divalent cations (Begg et al., 2015).

Accumulation of Cd in the edible parts of crop plants involves a number of steps, including uptake into the root cells, radial transport across the root cells and loading into the xylem, long-distance transport via the xylem and phloem, and transfer into the seeds or other types of storage organs (Clemens and Ma, 2016). This review focuses on the genetic basis for Cd uptake and transport by plants as this will be critical for Cd management through development and release of low-Cd accumulating cultivars. Many membrane transporters responsible for Cd transport have been identified in recent years (Table 9), primarily in the model dicotyledonous plant species *Arabidopsis thaliana* and the monocotyledonous crop species rice (*Oryza sativa*).

Two types of approaches are often employed in the studies to understand the molecular and genetic mechanisms for the transport and accumulation of mineral elements (e.g. Cd), i.e. reverse genetics and forward genetics. In reverse genetics, putative genes are guessed based on homology and phylogenetic relationship with known transporter genes, usually in other organisms or plant species. These are then knocked out or knocked down in the test plant species to observe changes in specific phenotypes (e.g. Cd uptake or translocation) from the wild-type plants. In forward genetics, variations in phenotypes are established first, e.g. between mutants and wild type or among plant germplasms. Genetic analyses are conducted to find the causative genes responsible for the phenotypes. Investigations of natural variation among germplasm (e.g. natural accessions or different crop cultivars) are particularly useful, because they can lead to identification of gene alleles with variation in the gene function, providing key information for marker-assisted molecular breeding of crop plants with improved traits. In the following sections, key transporters involved in Cd uptake, sequestration and translocation in plants are reviewed.

6.1 Mechanisms of cadmium uptake by roots

Zinc iron-regulated proteins (ZIPs) are a family of transporters for divalent transition metals such as Fe(II), Zn, Mn and Cd. Using a reverse-genetic approach, Vert et al. (2002) showed that AtIRT1, a member of the ZIPs, is the major transporter for Fe(II) uptake into the roots of *A. thaliana* under Fe deficiency. The AtIRT1 protein is localized to the plasma membranes and the gene is expressed in the external cell layers of the root, with a strong induction by Fe deficiency. These are important features of AtIRT1 as a key transporter for Fe(II) acquisition from the rhizosphere.

Table 9 Transporters involved in Cd uptake and translocation in plants.

Transporter	**Plant species**	**Functions**	**References**
AtIRT1	*A. thaliana*	Uptake of Fe(II), Zn, Mn and Cd into root cells under Fe-deficient conditions	Connolly et al. (2002), Eide et al. (1996), Korshunova et al. (1999), and Vert et al. (2002)
AtNRAMP1	*A. thaliana*	Uptake of Fe(II), Mn and possibly Cd into root cells under Fe replete conditions	Cailliatte et al. (2010) and Castaings et al. (2016)
OsNRAMP5	Rice	Uptake of Mn and Cd into root cells	Ishikawa et al. (2012, b), Sasaki et al. (2012), and Yang et al. (2014)
OsNRAMP1	Rice	Contributes to the uptake of Cd into root cells	Takahashi et al. (2011) and Chang et al. (2020)
OsIRT1 and OsIRT2	Rice	Possible involvement in the uptake of Fe(II) and Cd into root cells under Fe-deficient conditions	Ishimaru et al. (2012) and Nakanishi et al. (2006)
OsCd1	Rice	Uptake of Cd, and possibly also Mn, into root cells	Yan et al. (2019)
HvNRAMP5	Barley	Uptake of Mn and Cd into root cells	Wu et al. (2016)
NtNRAMP5	Tobacco	Possible involvement in the uptake of Mn and Cd into root cells	Tang et al. (2017b)
AtHMA3	*A. thaliana*	Tonoplast transporter for Cd, Zn, Co and Pb	Chao et al. (2012) and Morel et al. (2009)
OsHMA3	Rice	Tonoplast transporter for Cd, Zn	Liu et al. (2020), Miyadate et al. (2011), Sui et al. (2019), Ueno et al. (2010), and Yan et al. (2016)
GmHMA3	Soybean	Tonoplast transporter for Cd, Zn	Wang et al. (2012)
BrHMA3	*B. rapa*	Tonoplast transporter for Cd	Zhang et al. (2019)

NcHMA3 (TcHMA3)	*Noccaea caerulescens*	Tonoplast transporter for Cd, Zn with high expression in leaf cells	Ueno et al. (2011)
AtHMA2	*A. thaliana*	Efflux transporter for xylem loading of Zn and Cd	Hussain et al. (2004) and Wong and Cobbett (2009)
AtHMA4	*A. thaliana*	Efflux transporter for xylem loading of Zn and Cd	Chen et al. (2018c), Hussain et al. (2004), Mills et al. (2003, 2005), Verret et al. (2004), and Wong and Cobbett (2009)
OsHMA2	Rice	Influx or efflux (?) transporter mediating root-to-shoot translocation and intervascular transfer of Zn and Cd in the nodes	Satoh-Nagasawa et al. (2012), Takahashi et al. (2012), and Yamaji et al. (2013)
HvHMA2	Barley	Possible involvement in xylem loading of Zn and Cd	Mills et al. (2012)
AhHMA4	*A. halleri*	Efflux transporter for xylem loading of Zn and Cd	Hanikenne et al. (2008)
NtHMA4.1, NtHMA4.2	Tobacco	Efflux transporter for xylem loading of Zn and Cd	Liedschulte et al. (2017)
OsZIP7	Rice	Influx (?) transporter mediating root-to-shoot translocation and intervascular transfer of Zn and Cd in the nodes	Tan et al. (2019)
OsLCT1	Rice	Efflux transporter mediating intervascular transfer of Cd	Uraguchi et al. (2011)
OsCCX2	Rice	Possible efflux transporter mediating intervascular transfer of Cd	Hao et al. (2018)

Not only does AtIRT1 transport Fe(II), but it can also transport several divalent cations including Zn, Mn and Cd (Eide et al., 1996; Korshunova et al., 1999; Vert et al., 2002). Knockout of the *AtIRT1* gene in *A. thaliana* resulted in a greatly decreased Cd uptake under Fe-deficient conditions, and rendered the mutant more tolerant to Cd exposure (Vert et al., 2002). In contrast, overexpression of *AtIRT1* driven by the cauliflower mosaic virus 35S promoter increased Cd uptake by *A. thaliana* roots (Connolly et al., 2002). These results establish AtIRT1 as a key transporter for Cd uptake into the roots of *A. thaliana*, at least under Fe deficiency conditions.

It has been widely reported that Fe deficiency increases Cd accumulation in diverse plant species that may be related to this transporter (Cohen et al., 1998; Lombi et al., 2002a; Rodecap et al., 1994; Su et al., 2013). This observation can be explained by the fact that *IRT1* expression is strongly upregulated by Fe starvation, leading to an enhanced capacity for the uptake of not just Fe(II), but also Cd, Zn and Mn. Therefore, maintaining a sufficient supply of Fe to crop plants is important for preventing excessive Cd accumulation. It is possible to alter the substrate selectivity of IRT1 by changing the amino acid residues of the protein. For example, by replacing glutamic acid residue at position 103 in AtIRT1 with alanine selectively eliminated its ability to transport Zn (Rogers et al., 2000). Ideal variants of IRT1 would be to discriminate against Cd without affecting the transport abilities for essential micronutrients. Such variants are yet to be found (Rogers et al., 2000).

As a graminaceous plant species, rice possesses the Strategy II system for Fe acquisition (i.e. via phytosiderophore secretion and the uptake of Fe(III)-phytosiderophore complexes). However, rice also possesses partial components of the Strategy I system, with both OsIRT1 and OsIRT2 being functional with regard to Fe(II) transport activities (Ishimaru et al., 2006). Both OsIRT1 and OsIRT2 are also able to transport Cd when the genes are expressed in yeast (Nakanishi et al., 2006). It is possible that OsIRT1 and OsIRT2 may contribute to Cd uptake in rice under Fe-deficient conditions (Nakanishi et al., 2006), although the contribution may be minor (Clemens et al., 2013). Overexpression of *OsIRT1* increased Fe and Zn accumulations in rice grown under field conditions, but increased Cd accumulation only when the external Cd supply was very high (Lee and An, 2009).

Natural Resistance Associated Macrophage Proteins (NRAMPs) are another family of divalent cation transporters. Several NRAMP proteins from *A. thaliana* show transport activities for Mn, Cd and Fe(II) when expressed in yeast (Cailliatte et al., 2009; Thomine et al., 2000). AtNRAMP1 is a plasma membrane transporter with a high affinity for Mn, and is essential for Mn uptake by *A. thaliana* roots under low Mn conditions (Cailliatte et al., 2010). Mutation in AtNRAMP1 increases Cd tolerance, probably as a result of decreased Cd uptake (Cailliatte et al., 2010). AtNRAMP1 also contributes to Fe(II) uptake under Fe replete conditions, thus complementing the role of AtIRT1 in taking up Fe(II) under Fe deficiency conditions (Castaings et al., 2016). It is possible that AtNRAMP1 may be a key transporter for Cd uptake under Fe-sufficient conditions.

In rice, OsNRAMP5 is a major transporter for Mn and Cd uptake into the roots (Ishikawa et al., 2012; Sasaki et al., 2012; Yang et al., 2014). *OsNRAMP5* is expressed predominantly in rice roots and the protein is polarly localized at the plasma membranes of the distal side of both exodermis and endodermis cells, a localization pattern consistent with its role in the influx of Mn and Cd into the cells (Sasaki et al., 2012). Knockout of *OsNRAMP5* by T-DNA insertion greatly decreased short-term influx of Mn and almost completely abolished short-term influx of Cd into the roots. In both hydroponically and soil-grown plants, the mutant accumulated much lower levels of Mn and Cd in the roots, shoots and grains than wild-type plants. Knockout of *OsNRAMP5* also decreased Fe accumulation in the shoots of rice, although to a smaller extent than for Mn and Cd (Sasaki et al., 2012). Increasing Mn concentration in the hydroponic solution decreased Cd uptake by wild-type rice plants, but not in the *OsNRAMP5* mutant, indicating that Mn competes with Cd uptake via the OsNRAMP5 transporter (Yang et al., 2014). Using a forward-genetic approach, Ishikawa et al. (2012) isolated three ion-beam irradiated mutants of rice with a grain Cd concentration only about 3% of that in the wild type. The mutants also showed >90% reduction in the accumulation of Mn in rice shoots. They found that mutations in *OsNRAMP5* gene were responsible for the mutant phenotypes, further confirming the critical role of OsNRAMP5 in the uptake of Mn and Cd. Among the three mutants, two showed similar plant growth and grain yields to the wild-type cultivar under field conditions, suggesting that the decreased Mn uptake did not cause Mn deficiency and yield losses. This result is different from those of Sasaki et al. (2012) and Yang et al. (2014), who found decreased plant growth in the T-DNA insertion *OsNRAMP5* mutant under low levels of Mn supply. The difference may be attributed to different mutation alleles of *OsNRAMP5*.

Within the NRAMP family, OsNRAMP1 can also transport Cd when the gene is expressed in yeast (Takahashi et al., 2011). *OsNRAMP1* was mainly expressed in rice roots and the expression was greatly induced by Fe deficiency. Overexpression of *OsNRAMP1* in rice increased Cd uptake by roots (Takahashi et al., 2011). Knockout of *OsNRAMP1* resulted in significant decreases in root uptake of Cd and Mn and their accumulation in rice shoots and grains, suggesting that OsNRAMP1 also contributes to Cd and Mn uptake in rice (Chang et al., 2020).

HvNRAMP5 in barley is a close homolog of *OsNRAMP5*. *HvNRAMP5* is mainly expressed in the outer cell layers of barley roots and encodes a plasma membrane transporter protein with transport activities for Mn and Cd, but not for Fe(II) or Zn (Wu et al., 2016). Knockdown of *HvNRAMP5* gene expression by RNA interference (RNAi) resulted in significant reductions in the uptake of Mn and Cd, indicating its important role in the uptake of the two metals in barley roots (Wu et al., 2016). Compared with rice, barley roots took up smaller amounts of Mn per unit of root biomass, which can be attributed to a lower expression level of *HvNRAMP5* than *OsNRAMP5* (Wu et al., 2016).

In hydroponic experiments, root uptake of Cd in wheat and maize were lower than that by rice, particularly when Cd concentrations in the solution were low, but environmentally more relevant (Sui et al., 2018). The maximum influx velocity ($V_{\max}$) of Cd in wheat and maize was only 15% and 45%, respectively, of that in rice, suggesting a lower uptake capacity in the former two plant species. This difference could be explained by much lower (by 4–5-fold) absolute expression levels of *TaNRAMP5* in wheat roots and *ZmNRAMP5* in maize roots than that of *OsNRAMP5* in rice roots (Sui et al., 2018). In addition, although both TaNRAMP5 and ZmNRAMP5 could transport Mn and Cd when expressed in yeast, the transport activities were found to be lower than those of OsNRAMP5. TaNRAMP5 and ZmNRAMP5 may be involved in Cd uptake in wheat and maize, which would need to be ascertained by knocking out the genes in the two plant species.

Tobacco (*Nicotiana tabacum* L.) is a Cd accumulator, and smoking of tobacco contributes considerably to Cd exposure in the smokers (Clemens et al., 2013; Lugon-Moulin et al., 2004). NtNRAMP5 is a plasma membrane transporter with transport activities for Mn and Cd (Tang et al., 2017b). Allelic variation of *NtNRAMP5* exists among different tobacco cultivars. A low-Cd accumulating cultivar of tobacco was found to possess a truncated version *NtNRAMP5*, which showed little transport activities for Mn and Cd (Tang et al., 2017b). This allele has the potential for use in breeding low-Cd tobacco.

Recently, Yan et al. (2019) identified a new Cd transporter in rice, OsCd1, which belongs to the major facilitator family (MSF). The gene was found to underlie a grain Cd QTL on chromosome 3 from a genome-wide association study (GWAS) study of 127 rice cultivars. The gene encodes a plasma membrane transporter able to transport Cd when expressed in yeast, and is mainly expressed in the exodermis, cortex, endodermis and parenchyma cells in the stele of roots. Knockout of *OsCd1* gene decreased Cd concentrations in the roots and shoots by approximately 20–50%, and grain Cd concentration by 15–30%. The knockout lines also accumulated lower levels of Mn and showed reduced growth and fertility. Among rice cultivars, haplotype with aspartic acid at the 449th position ($\text{OsCd1}^{\text{D449}}$) showed a greater Cd transport ability than that with valine at the same position ($\text{OsCd1}^{\text{V449}}$). Interestingly, most of the Indica cultivars possess the $\text{OsCd1}^{\text{D449}}$ haplotype, whereas Japonica cultivars possess the weaker $\text{OsCd1}^{\text{V449}}$ haplotype. This difference may be one of the reasons for generally higher Cd accumulation in Indica cultivars than in Japonica cultivars (Yan et al., 2019). This study shows that OsCd1 contributes to Cd uptake by rice roots, although its contribution is relatively small compared with OsNRAMP5.

6.2 Translocation of cadmium within the plant to food organs

Root-to-shoot translocation is a key determinant of Cd accumulation in the aerial parts of plants, including grain. Among a panel of rice cultivars, Cd concentrations in the shoots correlated strongly with Cd concentrations in the xylem sap (Uraguchi et al., 2009). Similarly, grain Cd concentrations in 100 accessions of barley correlated significantly with root-to-shoot translocation (Wu et al., 2015). Grafting experiments with eggplant, soybean and potatoes showed that the root stock controls the efficiency of Cd translocation from the roots to shoots and, consequently, the accumulation of Cd in the shoots (Arao et al., 2008; Mengist et al., 2018; Mori et al., 2009; Sugiyama et al., 2007b). Translocation of Cd from the roots to shoots depends on several factors, most importantly the strength of vacuolar sequestration, the processes of xylem loading, and intervascular and xylem-to-phloem transfer.

6.2.1 Vacuolar sequestration affecting cadmium translocation

Following the uptake of Cd into the root cells, a portion of Cd is transported into the vacuoles. Vacuolar sequestration of Cd helps reduce its cytotoxicity and decrease its mobility for translocation from the roots to the other plant tissues. Recent studies have identified HMA3 (Heavy Metal Associated 3), belonging to the P_{1B} subgroup of the P-type ATPase family, as a key transporter for vacuolar sequestration of Cd. Importantly, variations in the *HMA3* coding sequence can explain a large portion of the natural variation in Cd translocation among different cultivars or accessions within the same plant species. This information paves the way for breeding low-Cd accumulating crop cultivars.

In *A. thaliana*, AtHMA3 is a tonoplast transporter for Cd, Zn, Co and Pb (Gravot et al., 2004; Morel et al., 2009). Mutation of *AtHMA3* increased the sensitivity to Cd and Zn, whereas overexpression of *AtHMA3* improved plant tolerance to Cd, Zn, Co and Pb (Morel et al., 2009). The overexpression of *AtHMA3* in plants led to more Cd accumulation in the roots. Variation in the coding region of *AtHMA3* has a large effect on Cd accumulation in the leaves of *A. thaliana* (Chao et al., 2012). Among 349 natural accessions of *A. thaliana* grown under the same greenhouse conditions, leaf Cd concentration varied by fourfold. Using a GWAS and linkage mapping, Chao et al. (2012) identified *AtHMA3* as the sole major locus responsible for the variation in leaf Cd accumulation. Sequencing of *AtHMA3* genes from 149 accessions of *A. thaliana* revealed the presence of ten major protein haplotypes of AtHMA3, among which five are active and the other five are inactive (i.e. weak or loss-of-function). Accessions possessing inactive AtHMA3 have significantly higher Cd concentrations in the leaves than those with active AtHMA3, due to the different abilities to sequester Cd in the roots (Chao et al., 2012).

In rice, OsHMA3 is also a key determinant of Cd accumulation in the shoots and grains. Similar to *AtHMA3*, OsHMA3 is localized to the tonoplast with transport activities for Cd and, possibly, also Zn (Cai et al., 2019; Miyadate et al., 2011; Sasaki et al., 2014; Ueno et al., 2010; Yan et al., 2016). The gene is predominantly expressed in the roots. Knockout or knockdown of *OsHMA3* leads to a higher sensitivity to Cd toxicity and elevated translocation of Cd from the roots to the shoots (Ueno et al., 2010). In contrast, overexpression of *OsHMA3* enhanced Cd tolerance and greatly decreased root-to-shoot translocation of Cd (Lu et al., 2019; Sasaki et al., 2014; Ueno et al., 2010). Using bi-parental mapping populations generated from crosses between high- and low-Cd accumulating rice cultivars, several weak or loss-of-function alleles of *OsHMA3* have been identified, which causes high root-to-shoot Cd translocation and high Cd accumulation in the shoots and grains (Miyadate et al., 2011; Sui et al., 2019; Ueno et al., 2010). Among different OsHMA3 protein haplotypes present in rice accessions, a single amino acid mutation at the 80th or 280th position, or a deletion of 14 amino acid residues in the ATP-binding domain result in total or partial loss of function to transport Cd into the vacuoles for sequestration (Sui et al., 2019; Ueno et al., 2010; Yan et al., 2016). Using positron-emitting ^{107}Cd tracer to monitor real-time distribution of Cd, Ishikawa et al. (2011) showed that rice cultivars possessing weak or null alleles of *OsHMA3* transported Cd from the roots to the shoots much more rapidly than cultivars with functional *OsHMA3*. In addition to coding region variation, variation in the promoter of *OsHMA3* among rice cultivars can cause variation in the expression level of the gene and possibly also affects Cd translocation (Liu et al., 2020).

The role of HMA3 in controlling in Cd translocation has also been confirmed in soybean (*Glycine max* (L.) Merr). A major quantitative trait locus (QTL) controlling Cd concentration in soybean seeds explains 57% of the phenotypic variation in a mapping population generated from a cross between a high-Cd and a low-Cd cultivar (Jegadeesan et al., 2010). The gene for this QTL has been identified as *GmHMA3*; the two variants of *GmHMA3* are identical except at the 608th position with glycine in the low-Cd cultivar and glutamic acid in the high-Cd cultivar (Wang et al., 2012). In a yeast assay, this single amino acid substitution from glycine to glutamic acid resulted in a loss of the transport activities for Cd and Zn (Wang et al., 2012).

Brassica rapa (B. rapa) includes some important vegetables widely consumed in Asian countries, including Chinese cabbage (*B. rapa*, ssp. *pekinensis*) and pak choi (*B. rapa*, ssp. *chinensis*). *Brassica rapa* and some other vegetables in the Brassicaceae (Cruciferae) family are known to have a high capacity to accumulate Cd in the edible parts (Kuboi et al., 1986). A recent study by Zhang et al. (2019) showed that the coding region variation in *BrHMA3* explains >80% of the variation in the root-to-shoot translocation of Cd among 64 *B. rapa* accessions and in a F_2 population. Five full-length and four truncated protein haplotypes of *BrHMA3* coding sequence are present in the 64 *B. rapa* accessions, with the truncated variants incapable of transporting Cd. *Brassica rapa* accessions possessing truncated BrHMA3 haplotypes have much higher root-to-shoot translocation and higher shoot Cd concentrations than those with full-length haplotypes.

Although root uptake of Cd in wheat (*Triticum aestivum*) appears to be smaller than that in rice, root-to-shoot translocation of Cd in wheat is considerably higher than that in rice, suggesting that wheat roots may have a smaller capacity to sequester Cd (Sui et al., 2018). Using near-isogenic lines of durum wheat (*Triticum turgidum* var. *durum*) differing in seed Cd accumulation, Harris and Taylor (2013) showed that the difference can be solely attributed to root-to-shoot translocation of Cd, and is not related to root uptake of Cd. Genetic mapping has identified a major QTL on chromosome 5B of durum wheat with low Cd accumulation being dominant over high Cd accumulation; this QTL explains >80% phenotypic variation in seed Cd concentration (Clarke et al., 1997b; Wiebe et al., 2010). The causal gene for this QTL has been identified as *TdHMA3-1* (Maccaferri et al., 2019). Overexpression of a functional *OsHMA3* in wheat greatly reduced Cd translocation from the roots to the shoots and Cd accumulation in wheat grain (Zhang et al., 2020).

From the studies described above, it is clear that natural variation in the *HMA3* coding region controlling Cd translocation to and accumulation in the shoots is a conserved mechanism across different plant species. Although HMA3 can transport multiple divalent cations, allelic variations in *HMA3* appear to affect mainly Cd, with little effect on the accumulation of Zn and other metals in the shoots (Ueno et al., 2010; Zhang et al., 2019). There is some evidence that AtHMA3 and OsHMA3 are involved in Zn storage in the root vacuoles (Cai et al., 2019; Chao et al., 2012). However, uptake and translocation of Zn involve more transporters, which are tightly controlled in response to the cellular Zn status (Lu et al., 2019; Sasaki et al., 2014). This tight regulation probably overrides the effect of HMA3 on Zn translocation. The lack of a strong linkage between Cd and Zn is advantageous as it allows breeding of low-Cd crop cultivars without adversely affecting seed Zn concentrations.

6.2.2 Xylem loading and root-to-shoot translocation

Cadmium in the rhizosphere can move into the stele for translocation *via* the apoplastic or symplastic pathways. In the apoplastic pathway, Cd transverses through the cell wall space to the stele without being taken up into the cells. The apoplastic pathway is stopped by the formation of the Casparian strip in the endodermal cells, except in the root tips and young root zone where the Casparian strip has not yet fully formed or in the regions where lateral roots branch out of the main root and break through the Casparian strip. In the symplastic pathway, Cd is taken up into the cells and moves across the root cells via the plasmodesmata, before being extruded from the pericycle and xylem parenchyma cells into the xylem vessels (xylem loading). The relative contributions of the two pathways are unknown, although the relative contribution of the apoplastic pathway may increase with increasing concentration of Cd in the rhizosphere (Lux et al., 2011). On the other hand, exposure to relatively high concentrations of Cd appears to promote the formation of the Casparian strip and the suberin lamellae coating of the endodermal cells closer to the root apex, thus restricting the apoplastic pathway (Lux et al., 2011; Schreiber et al., 1999).

In some plant species, such as rice, the Casparian strips are formed in both the exodermal and endodermal cell layers. In the mature root zone, the cortical cells between the exodermal and endodermal cell layers are often ruptured as a result of the formation of the aerenchyma, and therefore become the apoplastic space. In this case, solutes can move from the rhizosphere to the stele via the combined symplastic and apoplastic pathways, or "the coupled trans-cellular pathway" (Barberon and Geldner, 2014; Sasaki et al., 2016). In this route, ions are taken up into the exodermal and endodermal cells by influx transporters and extruded via efflux transporters, with the two types of transporters being polarly localized to the distal and proximal sides of the plasma membranes, respectively (Sasaki et al., 2016). Between the exodermal and endodermal cell layers, ions move in the apoplastic space. One example is Mn, which is transported into the stele through this combined pathway via the influx transporter *OsNRAMP5* and the efflux transporter *OsMTP9* (Metal Tolerance Protein 9) (Sasaki et al., 2012; Ueno et al., 2015). While *OsNRAMP5* is also a major transporter for Cd, *OsMTP9* does not transport Cd. Therefore, transporters for Cd efflux from the exodermal and endodermal cells remain unknown.

In the symplastic pathway, efflux of metal ions from the pericycle and xylem parenchyma cells inside the stele allows the ions to be loaded into the xylem vessels for translocation to the shoot tissues. In *A. thaliana*, AtHMA2 and AtHMA4 are the key efflux transporters responsible for the loading of Zn and Cd into the xylem (Hussain et al., 2004; Mills et al., 2003, 2005; Verret et al., 2004; Wong and Cobbett, 2009). Both genes are expressed predominantly in the vascular tissues of roots, stems and leaves. Mutation of *AtHMA4* decreased the translocation of Cd to the shoots by 40%, while mutations of both *AtHMA2* and *AtHMA4* reduced Cd translocation by as much as 98% (Wong and Cobbett, 2009). The double mutant also showed severe Zn deficiency symptoms (Hussain et al., 2004). *AtHMA4* single mutant and *AtHMA2 AtHMA4* double mutant were more sensitive to Cd and Zn toxicity, suggesting that the two transporters are also important for tolerance to Cd and Zn (Verret et al., 2004; Wong and Cobbett, 2009). *AtHMA4* appears to play a larger role than *AtHMA2*, although there is a degree of functional redundancy between the two transporters. Overexpression of *AtHMA4* increased Cd and Zn translocation to the shoots (Verret et al., 2004). Furthermore, allelic variation in *AtHMA4* causes variation in leaf Zn concentration among different accessions of *A. thaliana*, with weak or null alleles leading to low Zn accumulation in the leaves (Chen et al., 2018c). Allelic variation in *AtHMA4* may also affect Cd accumulation in the leaves, although this was not reported in the study of Chen et al. (2018c). There are two homologous *HMA4* genes in tobacco. Mutations of both genes resulted in >90% decrease in the root-to-shoot translocation of Cd, but also affected plant growth severely (Liedschulte et al., 2017). In the Zn and Cd hyperaccumulator *Arabidopsis halleri*, AhHMA4 also plays a crucial role in Zn and Cd translocation to the shoots, as well as the tolerance to the two metals (Hanikenne et al., 2008).

OsHMA2 in rice is also a transporter for Zn and Cd and is likely involved in the translocation of these two metals (Satoh-Nagasawa et al., 2012; Takahashi et al., 2012; Yamaji et al., 2013). The gene is expressed in the roots and the nodes of rice plants, and the protein is localized to the plasma membranes of the pericycle cells in the roots and the phloem region in the nodes (Yamaji et al., 2013). Mutation of *OsHMA2* gene decreased root-to-shoot translocation of Zn and Cd (Satoh-Nagasawa et al., 2012; Takahashi et al., 2012). Yamaji et al. (2013) observed decreased concentrations of Zn and Cd in the upper nodes and reproductive organs of the *OsHMA2* mutants compared with wild-type plants. There is disagreement as to whether OsHMA2 is an efflux transporter allowing Zn and Cd to be loaded into the xylem (Satoh-Nagasawa et al., 2012; Takahashi et al., 2012), or an influx transporter for the uptake of Zn and Cd into the pericycle cells in the roots and the phloem cells in the node for redistribution to the root tips and the reproductive organs (Yamaji et al., 2013). HvHMA2 from barley can transport Zn and Cd when expressed in yeast, while expression of *HvHMA2* in the *A. thaliana AtHMA2 AtHMA4* double mutant suppresses the Zn-deficient phenotype, suggesting that HvHMA2 could play a role in root-to-shoot translocation of Zn and Cd (Mills et al., 2012). Similarly, TaHMA2 from wheat may also be involved in Zn and Cd translocation (Tan et al., 2013).

OsZIP7 is an influx transporter for Zn and Cd localized to the plasma membranes of the pericycle in the roots and the parenchyma cells in the vascular bundles in the nodes of rice (Tan et al., 2019). Its distribution pattern appears to be similar to that of OsHMA2. The expression of *OsZIP7* gene was induced greatly by Zn deficiency. Knockout of this gene reduced the distribution of Zn and Cd from the roots to the shoots (Tan et al., 2019).

In rice, a defensin-like protein, named OsCAL1, is expressed mainly in the root exodermis and the xylem parenchyma cells and acts by chelating Cd in the cytosol and facilitating Cd secretion to extracellular spaces for translocation to the shoots, presumably via a unknown transporter (Luo et al., 2018). Surprisingly, OsCAL1 affects Cd accumulation in the shoots only without affecting Cd concentration in rice grain.

With regards to chelation of Cd, it is well known that the thiol-rich peptides phytochelatins (PCs) play a crucial role in complexing Cd and reducing its cytotoxicity (Ha et al., 1999; Howden et al., 1995). How complexation with PCs affects Cd translocation is less clear. Wong and Cobbett (2009) showed a significantly higher translocation of Cd from the roots to the shoots in PC synthase mutants compared with wild-type plants of *A. thaliana*, suggesting that complexation of Cd by PCs reduces its mobility for translocation. In contrast, Gong et al. (2003) reported that expression of the wheat PC synthase gene *TaPCS1* in the *A. thaliana* PCs mutant background increased Cd translocation to the shoots. The different results could be partly due to the different levels of Cd used in the experiments, with Gong et al. (2003) using a toxic level of Cd concentration (20 μM) compared with an environmentally more relevant level (0.2 μM) in the study by Wong and Cobbett (2009). In rice, mutants of *OsPCS1* accumulated lower levels of Cd in the leaves and grain than wild-type plants when grown on a soil containing a low level of Cd, suggesting that PCs promote Cd mobility in rice plants (Uraguchi et al., 2017).

6.2.3 Intervascular and xylem-to-phloem transfer of cadmium

Using radioactive ^{109}Cd tracer fed through roots, cut stems or flag leaves of rice, Tanaka et al. (2007) estimated that 91–100% of Cd accumulated in the grain was delivered via the phloem. This means that Cd has to be transferred from the xylem to the phloem at some point during its long-distance translocation from the roots to the grains. Cadmium is present in the phloem saps collected from rice and *B. napus*, probably as complexes with thiol-rich peptides (Kato et al., 2010; Mendoza-Cozatl et al., 2008; Tanaka et al., 2003). The concentrations of Cd in the phloem sap were lower than those in the xylem sap in rice (Tanaka et al., 2003), but the opposite was found in *B. napus* (Mendoza-Cozatl et al., 2008). Using a positron-emitting tracer imaging system, Fujimaki et al. (2010) showed that the ^{107}Cd tracer fed to rice roots arrived at the panicles 7 h after feeding, which was faster than the arrival of the tracer in the leaf blades (36 h). Moreover, rice nodes showed the most intensive ^{107}Cd accumulation in the shoot, suggesting that they are the central organ controlling the distribution of Cd to different tissues. Nodes in cereal crops are enlarged to accommodate different types of expanded vascular bundles, which control the distribution of nutrients (and contaminants such as Cd) to leaves, upper nodes or the reproductive organs (Yamaji and Ma, 2017). Enlarged vascular bundles in a node are connected with vascular bundles in the lower node and a leaf, whereas diffuse vascular bundles surround the enlarged vascular bundles and are connected to the upper node or panicle. In the nodes, portions of nutrients delivered from the roots or lower nodes via xylems of the enlarged vascular bundles are transferred across to the diffuse vascular bundles to be distributed to the upper nodes or panicles, a process called intervascular transfer (Yamaji and Ma, 2017). During the intervascular transfer, xylem-to-phloem transfer also occurs. In potatoes, Reid et al. (2003) used ^{109}Cd tracing to demonstrate that direct uptake of Cd from soil by stolons and tubers is negligible and that most of the Cd in the tuber was absorbed by the basal roots, translocated to stems and leaves in the xylem and rapidly loaded into the phloem which is the pathway for Cd movement to tubers. Experiments examining the kinetics of Cd uptake during growth and development supported these findings (Dunbar et al., 2003).

Several transporters play important roles in the intervascular and xylem-to-phloem transfer of Cd. The low-affinity cation transporter OsLCT1 is expressed in both the enlarged vascular bundles and the diffuse vascular bundles in rice nodes and is a plasma membrane efflux transporter for Cd (Uraguchi et al., 2011). Knockout of *OsLCT1* by RNAi did not affect the Cd concentration in the xylem sap, but decreased the Cd concentration in the phloem sap, suggesting that the transporter is involved in the xylem-to-phloem transfer of Cd. The RNAi lines accumulated about half of the Cd concentration in the grains of the wild-type rice. Although LCT1 is a transporter for broad-spectrum cations, including Ca, Mg, Mn, K and Cd (Clemens et al., 1998; Uraguchi et al., 2011), knockdown of *OsLCT1* appears to reduce the concentration of Cd in the grains only.

Not only is OsHMA2 involved in the root-to-shoot translocation of Cd and Zn, but it also takes part in the control of Cd and Zn distribution in rice nodes (Yamaji et al., 2013). The transporter is localized to the phloem parenchyma cells and companion cells in both the diffuse and enlarged vascular bundles in the node, probably functioning as an influx transporter to absorb Zn and Cd arriving from the xylem. Mutation of *OsHMA2* produced distinct phenotypes of reduced Zn and Cd distribution to both the panicle and the flag leaf (Yamaji et al., 2013). OsZIP7 appears to play a similar role to OsHMA2 in the intervascular transfer of Zn and Cd in the nodes (Tan et al., 2019). The putative cation/Ca exchanger OsCCX2 is another transporter involved in the intervascular transfer of Cd in rice node (Hao et al., 2018). This transporter was highly expressed in the xylem region of the enlarged vascular bundles, and knockout of this gene decreased Cd accumulation in rice grain by about 50%.

Identification of key genes and alleles involved in Cd uptake and translocation can provide targets for genetic engineering or marker-assisted breeding programs aimed at reducing Cd accumulation in the edible portions of food crops (see Section 7.5).

7. Managing cadmium in agricultural systems

7.1 Reducing cadmium inputs

Cadmium concentration in crops is related to the concentration of available Cd in the soil; therefore, it is important to reduce external inputs of Cd into agricultural soils to reduce risk of accumulation. Anthropogenic input of Cd into soils is described in detail in Section 2.2. In agricultural systems, in the absence of industrial contamination, the major inputs of Cd occur through application of phosphate fertilizer and lime (Sheppard et al., 2009). In areas near urban centers or intensive livestock production, application of biosolids or manures may also be major contributors locally. Management of inputs from these sources are discussed in detail in Section 1.3. Use of efficient fertilizer management practices in terms of source, timing and placement to reduce the fertilizer application rate required to optimize crop yield and quality will also reduce Cd inputs and may improve economics of production (Grant and Flaten, 2019).

As discussed in Sections 3 and 4, mobility and availability of Cd in the soil is strongly affected by factors including soil pH, CEC, and presence of Cl-based salinity. Therefore, the availability of anthropogenic Cd inputs will vary substantially from soil to soil. For example, in field studies on the Canadian prairies, Cd added in phosphate fertilizers over a 8-year period had a much greater effect on diethylenetriaminepentaacetic acid (DTPA)-extractable Cd and plant uptake on low pH soils with a low

CEC than on higher pH, carbonated soils with a high CEC (François et al., 2009; Grant et al., 2013; Lambert et al., 2007). Similarly, in pot studies plant availability of added Cd was lower on higher pH soils or soils where pH was adjusted to high levels than in low pH soils (Eriksson, 1989). Therefore, reducing Cd inputs may be a greater priority on sensitive soils where high availability of Cd inputs would be more likely to enter the food chain. The risk of mobilization of past Cd inputs through soil acidification should also be considered. Reducing inputs of Cd are unlikely to immediately manifest in lower crop Cd concentrations (Sparrow et al., 1993a), as the amounts added in inputs are small compared to the stock of Cd already present in soil (Section 5.2), and plants only take up very small proportions (<3%) of the recently applied Cd (Wiggenhauser et al., 2019). Hence, controlling Cd in agricultural systems by reducing Cd inputs will take decades or centuries to have effects on food Cd quality. It is interesting to note that reductions in Cd concentrations in wheat grain in Sweden in the period 1980–2003 took decades to be observed and were attributed to declining atmospheric inputs of Cd (Kirchmann et al., 2009).

While reducing anthropogenic inputs of Cd to soils can reduce the risk of excess accumulation over time, there are many soils throughout the world that have a naturally high level of available Cd (Section 2.1). The availability of Cd in soils with elevated geogenic Cd concentrations will vary with other soil characteristics, particularly soil pH. Plant-availability of geogenic Cd present in the soil tends to increase as soil pH decreases, increasing the risk of Cd movement from soil into the food chain (Liu et al., 2017). Management of naturally high Cd soils is problematic, since Cd inputs from weathering of parent rock/drift materials cannot be easily managed and the depth of Cd-enriched soil is usually great (Chavez et al., 2015). Addition of Zn (Section 7.3), production of non-food crops, or production of crop species and cultivars that are genetically low in Cd (Sections 7.4 and 7.5), liming to increase soil pH (Section 7.6.1) and addition of sorbents (Section 7.6.2) may be used to limit the risk of movement of geogenic Cd into the food chain.

7.2 Predicting high-risk cadmium soils

Uptake of Cd by crops is a function of the amount of Cd present in the soil, its availability and plant characteristics. However, total Cd in the soil is not necessarily an accurate measurement of risk of transfer into the food chain because much of the Cd is held in forms that are not immediately plant-available, as described in detail in Sections 3 and 4. Cadmium risk will be associated with high bioavailability in soils so the prediction of the portion of Cd that is available for uptake is important to assess the risk of Cd transfer from the soil into the food chain. A variety of different soil testing methods are used to estimate the plant-available Cd present in the soil. Most of these rely on the use of chemical extractants, which vary in their strength and in the portion of Cd that they will remove from the soil.

Cadmium is taken up by the plant root from the soil solution and the bioavailable fraction of Cd in the soil is normally considered that which is present in the soil solution and/or that which can be rapidly released into the soil solution. Analysis of the Cd concentration in pore water extracted from the soil by displacement, micro-tensiometers or centrifugation can identify the concentration of water-soluble Cd directly present in the bulk soil solution (Kumpiene et al., 2017; Lorenz et al., 1994; Meers et al., 2007b; Mitchell et al., 2000). In a study using over 50 soils from across Australia, Cd accumulation in cucumber shoots could be predicted from a measurement of Cd in pore water and free ion Cd^{2+} calculated from the soil solution composition (Lamb et al., 2016). However, separating porewater from soil is not a simple task and Cd concentrations are dependent on the method of separation.

The concentration present in the soil solution is important, but the ability of the soil to replenish the Cd extracted by the root over time is also relevant (Degryse et al., 2009b). The Cd removed by the soil solution by root uptake will be replenished by labile forms of Cd. Chemical extractants can be used to estimate the amount of bioavailable Cd in soils including that present in the soil solution and that which can readily replenish the depleted solution (Bolan et al., 2014). Single extractants that remove the Cd present in the soil solution and the highly labile forms include weak salt solutions such as 0.1 M or 0.01 M calcium chloride ($CaCl_2$), 0.1 M calcium nitrate ($Ca(NO_3)_2$), 1 M ammonium nitrate (NH_4NO_3), 0.1 M sodium nitrate ($NaNO_3$), and 1 M magnesium chloride ($MgCl_2$) (Meers et al., 2007a,b). Weak salts rely on desorption or ion exchange to release Cd^{2+} from the soil into the solution for analysis. Concentrations extracted by the Cl^- salt are normally higher than those extracted by the corresponding nitrate salt, since Cd will form stronger complexes with the Cl^- than the nitrate (NO_3^-) ion (McLaughlin et al., 2000b). However, the ionic strength of a 0.01 M XCl_2 (where X is a divalent cation) solution is similar to many soil solutions and so Cd in the extraction solution should be in equilibrium with the same pool of metals as the soil solution in the field. Extraction with a 0.01 M

$CaCl_2$ extract therefore provides a reasonable estimate of the Cd in the pore water of contaminated soils in the field (Degryse et al., 2003).

Organic acid-based extractants such as acetic acid, ammonium acetate or inorganic acids are more aggressive than weak salts and remove more Cd from soil (Meers et al., 2007a). Complex-based chelating agents such as DTPA solutions (0.005 M DTPA, 0.01 M $CaCl_2$, 0.1 M triethanolamine (TEA) (pH 7.3)) (Lindsay and Norvell, 1978; Norvell et al., 2000) and ethylenediaminetetraacetic acid (EDTA) solutions (0.5 M ammonium acetate (NH_4Ac), 0.5 M acetic acid (HAc), 0.02 M EDTA (pH 4.65)) that desorb the Cd from the soil and hold it in a complexed form have also been used to predict the plant-available portion of Cd in the soil. These extractants are said to simulate the metal chelating effects of root exudates. However, these synthetic chelates are much more stable than naturally occurring organic acids (Meers et al., 2007a).

Strong inorganic acids will release Cd that is more strongly held in the solid phase and provide an estimate of total Cd in the soil (McLaughlin et al., 2000b). Oxidation/reduction reactions can be used to release large amounts of Cd from the soil by oxidizing organic materials that bind metals or metal sulfides. Peroxide, hypochlorite or hot concentrated acid solutions including nitric acid (HNO_3), hydrochloric acid (HCl), perchloric acid ($HClO_4$) or hydrofluoric acid (HF) including *aqua regia* (1:3 HNO_3:HCl) are effective compounds for estimating total Cd in soils. The acid-based extractants including 0.5 M HNO_3 and 0.1 M HCl are more aggressive than the weak salts and are highly correlated with *aqua regia* digestion indicating that they reflect the total Cd content (Meers et al., 2007a). Reducing agents such as acidified hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$), acidified oxalate and dithionite/citrate solutions which often form part of sequential fractionation schemes for heavy metals can solubilize oxides and hydroxides of Al, Fe and Mn and release the Cd that they bind (McLaughlin et al., 2000b). In a comparison of a range of extractants, the amount of Cd measured differed with the extractant type but was highly correlated across extractants. The extraction efficacy was similar across soil types and was in the order aqua regia $\approx$ HCl $\approx$ HNO_3 $\approx$ HNO_3 $>$ EDTA (pH 4.65) $\geq$ acetic acid (Meers et al., 2007a).

In addition to chemical extractants, resin and resin-related method have been used to estimate plant-available Cd. Diffusive gradients in thin films (DGT) have been developed for *in situ* sampling of dissolved trace element ions in water, sediments, and soils (Degryse et al., 2009b; Nolan et al., 2005). The DGT technique is based on diffusion of dissolved trace element ions through a diffusive hydrogel layer and accumulation in a resin layer. The DGT devices are placed in soils for a defined time, during which ions from the soil solution accumulate in the resin layer. Then, the mass of the accumulated ion is measured and used for calculating ion fluxes and concentrations at the DGT–soil interface. The DGT technique is promising for estimation of plant-available Cd where the supply to the plant root is diffusion limited (McLaughlin et al., 1998c), which is often the case in soils (McLaughlin et al., 1998c). A detailed review on the processes affecting the performance of DGT-derived soluble ion concentrations in soils can be found in Degryse et al. (2009b). Under diffusion limited environments, where Cd concentration is relatively low, DGT or other resin systems may provide a good estimation of Cd availability for plant uptake (Liang and Schoenau, 1995). In pot studies using a range of contaminated and uncontaminated soils that were spiked with $CdCl_2$ and aged, Cd uptake by wheat was better predicted by 0.01 $CaCl_2$ and resin membrane extractable Cd than by 0.1 M HCl, or DTPA-extractable Cd (Lee and Zheng, 1994).

Some studies have used visible near-infrared reflective spectroscopy (VNIRS) as a rapid cost-effective non-destructive method of assessing concentrations of metals in soil (Soriano-Disla et al., 2013). In studies on two soils amended with paper mill biosolids and liming by-products, Cd assessed through VNIRS was highly correlated with DTPA-extractable or Mehlich-3-extractable Cd, with the relationship between Cd and soil organic matter being the major predictive mechanism (St. Luce et al., 2017). However, these indirect associations of Cd with infrared (IR)-visible soil components are not universally applicable across different soils so it is unlikely IR methods will be successful for predicting Cd bioavailability across a wide range of soils.

Sequential fractionation schemes are often used to evaluate the forms of Cd in soluble, adsorbed, precipitated, organic and occluded forms in soils (Section 3.1.2). Most schemes using increasingly strong extractants to sequentially remove more sparingly available forms of the metal with the bioavailability and solubility of Cd in the soil decreasing with each successive extraction step. Therefore, the "pools" of Cd should reflect differing availabilities. The major pools are generally considered in order of decreasing availability (1) exchangeable; (2) bound to carbonates; (3) bound to Fe and Mn oxides; (4) bound to organic matter; (5) residual forms. Sequential extraction techniques provide more detailed information about the forms in which Cd is retained in the soil but are not practically used for routine assessment of Cd risk in soils.

The validity of use of specific chemical extractants is usually evaluated by a comparison with bioassays to determine the relationship between the concentration of Cd extracted and the amount accumulated by organisms, most commonly plants. However, it is important to recognize that accumulation of Cd will differ among different plant types and plant parts, and be affected by environmental factors affecting plant growth, rooting and Cd availability. In a meta-analysis evaluating the relation between various measures of available Cd and Cd accumulation in cereal crops, total elemental concentration provided a poor indication of phytoavailability with $R^2 < 0.5$ for Cd (Menzies et al., 2007). DTPA and EDTA were also poor in predicting plant uptake ($R^2 < 0.5$). The neutral salt solutions tended to provide the best relationship between extractable Cd and Cd accumulation in the plant tissue, with $R^2 > 0.5$. In a study using 0.05 M EDTA-$(Na)_2$, 0.005 M DTPA, 0.0 5 M $CaCl_2$ and 1 M NH_4NO_3 as soil test reagents, on a biosolids-amended soil, extraction with DTPA gave the best overall prediction of crop Cd concentrations in lettuce, cabbage and potato tuber (Jackson and Alloway, 1991). In pot studies with a range of contaminated soils collected from Australia and the United States, $CaCl_2$-extractable Cd and effective Cd concentration (derived from DGT measurements after plant growth) were effective predictors of Cd uptake by wheat plants (Nolan et al., 2005). Therefore, while soil testing with various extractants may provide an indication of Cd risk in soils, other soil and environmental factors will also be important in affecting the availability of native Cd and Cd added through anthropogenic activity.

Predictive modeling may be used to incorporate information from soil testing with information on other soil and environmental factors that will influence Cd movement into plants (Tudoreanu and Phillips, 2004). While the amount of Cd present in the soil as measured by soil testing is important, the bioavailability of the Cd present is strongly affected by soil characteristics. Mineral weathering and acidification, redox reactions, complexation, biochemical processes, and CEC as influenced by clay content, organic matter and Fe and Al oxides can influence the forms and availability of Cd present and therefore its availability for plant uptake (Kumpiene et al., 2017). The distribution of Cd between the soil and the solution phase (as described by the K_d value) will affect the amount of Cd available for crop uptake. There is a huge range of K_d values for Cd in soil due to varying soil pH, CEC, organic matter content and ionic strength of the soil solution (Sauvé et al., 2000a; Sheppard et al., 2007). Therefore, models using total soil Cd and incorporating soil factors that influence K_d and Cd availability can be used to predict Cd risk. Soil pH and CEC are two of the dominating factors influencing availability. Cadmium sorption will normally be low in low pH soils and increases as pH increases (Section 4). In studies on both uncontaminated soils and soils that had been treated with biosolids, Cd accumulation in a range of crops could be predicted from:

$$\mathrm{Log}\left(\mathrm{Cd}_{\mathrm{crop}}\right) = \mathrm{a} + \mathrm{b}(\mathrm{soil\ Cd}) - \mathrm{c}(\mathrm{soil\ pH}) \tag{5}$$

with a, b and c varying with soils, climate and crop type and soil Cd being measured as total Cd in soil (McBride, 2002). In studies using paired soil and plant samples from contaminated sites in Belgium and France, the concentration of Cd in nettle and grass samples was shown to be best predicted by equations including *aqua regia* Cd and soil properties such as clay content, while $CaCl_2$-extractable Cd was a poor predictor (Boshoff et al., 2014). In a study of paired soil and wheat or barley grain samples in the UK, wheat grain Cd concentration could be predicted reasonably well with total soil Cd and pH ($R^2 = 0.53$), whereas it is more difficult to predict Cd concentration in barley grain, partly due to the generally lower levels of Cd accumulation in barley grain (Adams et al., 2004). For paddy rice, grain Cd concentration showed very weak correlation with either total soil Cd concentration or pH (Chen et al., 2018a; Simmons et al., 2008). This is because Cd availability in paddy soil is affected greatly by the redox status during grain-filling stage, which is in turn controlled by paddy water status in the field. Simmons et al. (2008) showed that 0.1 M $CaCl_2$-extractable Cd and soil pH determined on field moist samples, rather than air-dried soils, predicted rice grain Cd concentration much better ($R^2 = 0.64$). Measured Cd concentrations in 3000 samples from 5 field sites of brown rice collected in Taiwan were predicted very well ($R^2 > 0.8$) based on measured Cd and Zn concentrations in a 0.01 M $CaCl_2$ extract or based on a soil-plant transfer model using the acid extractable oil Cd content, pH, and CEC (Romkens et al., 2009).

In dryland soils, the presence of Cl^- salts can have a major effect on Cd uptake by plants. For irrigated crops, the Cl^- in the irrigation water can be a primary indicator of risk of Cd accumulation by plants. For example, using a data set of 134 sites in southern Australia, 0.01 M $CaCl_2$, 0.01 M $Ca(NO_3)_2$, Cd^{2+} activity (calculated) in 0.01 M $Ca(NO_3)_2$, 1.0 M NH_4NO_3, and 0.05 M EDTA were tested for their ability to predict tuber Cd concentrations in irrigated potato production (McLaughlin et al., 1999). A simple measurement of irrigation water Cl^- concentration explained 43% of the variation in tuber Cd concentrations, with Cd extracted by 0.01 M $CaCl_2$ explaining an additional 12%.

Finally, it is worth noting when reading the literature for soil testing for predicting Cd accumulation in crops that many studies do not meet the criteria suggested by McLaughlin et al. (1999) for a successful test, namely the soil test:

(1) should be relatively simple, inexpensive and robust;
(2) should be calibrated under field conditions across a wide range of soil types;
(3) should be independently validated;
(4) should account for the major environmental factors known to affect crop metal concentrations or toxic response to plants or organisms (for assessing current hazard or risk, i.e. diagnosis); and
(5) for prognosis, must be truly predictive, i.e. measurements prior to planting of the crop must be correlated against plant measurements at harvest, and not a correlation between measurements on soil and plant samples at the same point in time.

7.3 Zinc

Cadmium and Zn are chemically similar, however unlike Cd, Zn is an essential element both for plant and human nutrition. While Zn can be present at high concentrations in contaminated soils, it is frequently present at very low concentrations in agricultural soils and deficiencies may occur affecting both crop growth and human health (Alloway, 2009; Cakmak, 2008; Cakmak et al., 1996a). Application of Zn fertilizer is used to alleviate Zn deficiency in crops, increasing yield on Zn-deficient soils and potentially improving crop quality by increasing the Zn concentration in the edible portion of the plant (Cakmak, 2008; Cakmak et al., 1996b; Torun et al., 2001). Zinc availability is affected by soil characteristics including the total Zn content, soil pH and redox conditions, calcium carbonate and organic matter content, and concentrations of other trace elements, macronutrients and ligands that are able to form organo-Zn complexes (Alloway, 2009). Zinc deficiencies are most likely to occur on soils with low total Zn concentration, high organic matter content and on calcareous and/or high pH soils.

Applications of Zn fertilizer have been shown to increase, decrease or have no effect on Cd accumulation and concentration in plants, depending on the specific environmental conditions and the plant species involved. Zinc can compete with Cd adsorption and complex formation which will influence the concentration of Cd in the soil solution and hence its availability for plant uptake (Helmke, 1999; Tiller et al., 1979). At low concentrations of Cd, representative of most agricultural soils, Cd adsorption and complexation reactions will have a major influence on the distribution of Cd between the solid and soil solution phases and on the availability of Cd for plant uptake (Christensen and Huang, 1999; Degryse et al., 2009a; Loganathan et al., 2012). Zinc is usually present in soils at concentrations more than a hundred times higher than that of Cd (Green et al., 2017) and may compete with Cd for sorption sites, reducing Cd adsorption and increasing the solution Cd available for crop uptake although at normal to slightly contaminated level of Cd competitive effects may be relatively minor (Christensen, 1984a; Christensen and Huang, 1999). This increase in solution concentration could increase the availability of Cd for crop uptake.

However, many studies have demonstrated antagonism between Zn and Cd, with increasing soil or nutrient solution concentrations of Zn or foliar applications of Zn fertilizer leading to reduced accumulation of Cd in a wide range of crops including wheat (Grant and Bailey, 1998; Hart et al., 2002, 2005; Jiao et al., 2004; Oliver et al., 1994; Saifullah et al., 2016; Tavarez et al., 2015; Zhao et al., 2005), flax (Grant and Bailey, 1997; Jiao et al., 2004; Rojas-Cifuentes et al., 2012), lettuce and spinach (Chaney et al., 2009; McKenna et al., 1993) and potato (McLaughlin et al., 1995). Antagonism between Zn and Cd may reflect competition between the two ions for carriers involved in uptake and translocation within the plant (Section 6).

Both Cd and Zn are first taken up from the soil solution by the plant root, then loaded to the xylem, translocated to the shoots and moved to the seed through the phloem. Recent studies have shown that Cd and Zn share the same membrane transporters *HMA2* and *HMA4* for xylem loading and intervascular transfer (see Section 6). Competition between the two cations during translocation is therefore expected.

Effects of Zn on Cd accumulation in plants will be affected by the absolute and relative concentration of the two ions (Zare et al., 2018). Studies conducted at very high concentrations of Zn and Cd provide little useful information relevant to field situations as uptake at high concentrations can occur through a low-affinity uptake system that is not significant at environmentally relevant concentrations (Chaney, 2015). At very low Zn levels, which is common in some regions, Zn-deficient plants may lose root-cell plasma membrane integrity, allowing increased influx of Cd. Correction of Zn deficiency will therefore allow for greater control of Cd influx by the plant, reducing Cd concentrations the plant (Oliver et al., 1994).

Correcting Zn deficiency may also reduce upregulation of the Zn transporter, decreasing Cd uptake (Chaney et al., 2009; Talke et al., 2006; Zare et al., 2018). In addition, increases in crop biomass yield from Zn applications to deficient plants may decrease Cd concentration in the tissue through dilution/concentration effects. Therefore, addition of Zn to alleviate severe deficiency will usually decrease Cd accumulation in plants. In contrast, if Zn is not deficient for plant growth, additions of Zn may have little effect on Cd accumulation (Rojas-Cifuentes et al., 2012), although in some instances Cd concentration in seeds may still be reduced (Grant and Bailey, 1997; Jiao et al., 2004).

While Zn application has frequently been shown to reduce Cd concentration in a range of crops, it has been less effective in reducing accumulation in rice grain (Chaney, 2015). In some studies Zn application at low rates decreased xylem loading of Cd, with no further decrease occurring as rate of Zn increased further (Fontanili et al., 2016). Other studies have reported no effect or synergism between Zn and Cd in rice, with an increase in Zn increasing the translocation of Cd from the roots to the shoots especially at high Cd supply (Green et al., 2017). Observed differences may be because there are multiple transport systems involved in Cd uptake in rice making the relationship between Zn and Cd more complicated than in other crops (Arao and Ishikawa, 2006; Ishikawa et al., 2005; Ishimaru et al., 2012; Kashiwagi et al., 2009; Sasaki et al., 2012). Uptake of Cd via Zn carrier systems may be decreased as Zn concentration increases while uptake via Mn carrier systems may be unaffected by Zn concentration (Chaney, 2015; Sasaki et al., 2012).

7.4 Reducing plant uptake through species/cultivar selection

On soils where Cd availability is high, risk of Cd transfer into the food chain may be managed by growing fuel, fiber or ornamental crops that are not consumed in the diet. However, shifting production to non-food crops is not always a viable option. Therefore, production of food crops that accumulate low levels of Cd is desirable.

Crop species differ widely in their ability to absorb, accumulate and tolerate Cd (Bingham et al., 1975; Hocking and McLaughlin, 2000; Kuboi et al., 1986). Cadmium accumulation and distribution in plants is affected by factors under genetic control, including size and morphology of the root system, production of root exudates that can mobilize Cd, root association with microorganisms such as mycorrhizal fungi and root-colonizing bacteria, presence of intracellular binding sites, and the amount and activity of transport systems across cell membranes that mediate vacuolar sequestration, xylem loading and unloading, and phloem transport (see Section 6). In some crops, Cd may be readily taken up, but limited translocation from root to stem and to leaves and fruit leads to low concentrations in the fruits, storage roots/tubers and grains (Arao and Ishikawa, 2006; Florijn and Van Beusichem, 1993; Harris and Taylor, 2001, 2004; Hart et al., 2006; Tavarez et al., 2015).

Of food crops commonly traded internationally, sunflower, rice and durum wheat tend to accumulate higher concentrations in their edible portions than other crops, frequently containing more than 0.10 mg Cd kg^{-1} dry matter (Arao and Ishikawa, 2006; Li et al., 1997). The concentration of Cd in peanuts (Bell et al., 1997), potatoes (McLaughlin et al., 1997a; Öztürk et al., 2011), yams (Lalor, 2008), and soybeans (Arao and Ishikawa, 2006) are also of concern, particularly where they comprise a large portion of the diet. Flax accumulates high concentrations of Cd in the seed but does not make up a significant portion of the diet (Grant et al., 2000). Concentrations of Cd in spring wheat, barley, oat and maize are usually less than 0.10 mg kg^{-1} (Adams et al., 2004; Erdman and Moul, 1982; Guo and Marschner, 1996; Oliver et al., 1995).

Large genetic differences in Cd concentration may also occur among cultivars within a species. Natural genetic variation has been identified in many different crops including but not limited to asparagus bean (*Vigna unguiculata* subsp. *Sesquipedalis* L.) (Zhu et al., 2007), barley (Chang et al., 1982; Chen et al., 2007), carrot (Harrison, 1986), corn (maize) (Hinesly et al., 1978), cucumber (Harrison and Staub, 1986), common wheat (Gray et al., 2001), durum wheat (Clarke et al., 1997a,b), linseed (Grant et al., 2000; Hocking and McLaughlin, 2000), lettuce (Crews and Davies, 1985; Thomas and Harrison, 1991), pea (Rivera-Becerril et al., 2002), peanut (Bell et al., 1997; McLaughlin et al., 2000a), potato (McLaughlin et al., 1994b; Öztürk et al., 2011), rice (Arao and Ae, 2003; Arao and Ishikawa, 2006; Chi et al., 2018; He et al., 2006; Shi et al., 2009), ryegrass (Gray and McLaren, 2005), soybean (Arao and Ishikawa, 2006; Jegadeesan et al., 2010; Morrison, 2005) and sunflower (Li et al., 1995, 1997).

The physiology behind genetic differences among cultivars in Cd concentration in the grain has been identified in several crops. Distribution of Cd within the plant is influenced by transport from roots to the shoots *via* the xylem, transfer from the xylem to the phloem and transport through the phloem from sources to sinks (Clemens et al., 2013;

Riesen and Feller, 2005). Transport of Cd within the plant to storage organs appears to be largely phloem-mediated (Clemens et al., 2013; Dunbar et al., 2003; Reid et al., 2003; Tanaka et al., 2003, 2007). Differences among cultivars in Cd concentration may be in part related to differences in the abilities of plants to control movement of Cd from root to the xylem to the phloem and *via* the phloem to the seeds or tubers as discussed in Section 6.2.3 (Cakmak et al., 2000a,b; Hart et al., 2002, 2006; Hocking and McLaughlin, 2000). Accumulation of large amounts of Cd in the root may limit the accumulation of Cd in edible above-ground portions of the plant (Buckley et al., 1997; Sugiyama et al., 2007a,b). In studies where shoots and rootstocks from high and low accumulating soybean lines were recombined by grafting, rootstocks with a capacity to accumulate high amounts of Cd led to a reduction in the Cd concentration of seed, indicating that the accumulation of Cd in the seed was reduced by high accumulation in the root and was controlled by the rootstock cultivar (Sugiyama et al., 2007b). In two near-isogenic lines of durum wheat, the line with low Cd concentration in the seed had higher concentration in the root because the low Cd lines retained more Cd in the root and translocated less to the seed (Harris and Taylor, 2001, 2004; Hart et al., 2005, 2006; Tavarez et al., 2015). Similarly, rice cultivars with low grain Cd concentrations retain greater amounts of Cd in the root with chelation, vacuolar storage and adsorption reactions apparently reducing the Cd available for xylem transport to the upper plant (Uraguchi et al., 2009; Xu et al., 2017). Based on field trials in multiple environments (locations and years), Duan et al. (2017) identified 8 rice cultivars that were consistent in low accumulation of Cd in grain among a panel of 471 locally adapted high-yielding cultivars in southern China. These low-Cd cultivars can be readily grown in moderately contaminated paddy soils to ensure compliance with the grain Cd limit.

Genetic variability provides the opportunity for plant breeding to reduce the concentration of Cd in the crops produced (Clarke et al., 1997b; Grant et al., 2008). Plant breeding is an attractive method for changing the Cd concentration in crops as the benefit will persist in the seed and can reduce the requirement for other management techniques such as fertilization management or crop rotations. Selection programs for a low Cd content of various crops, including durum wheat, sunflower, rice and soybean have been established and low-Cd cultivars and hybrids identified and/or developed (Arao and Ae, 2001; Arao and Ishikawa, 2006; Clarke et al., 1997b; Jegadeesan et al., 2010; Li et al., 1997; Uraguchi and Fujiwara, 2013).

7.5 Decreasing cadmium accumulation in food organs by engineering and breeding new cultivars

Cadmium accumulation and distribution in crops is controlled by genetics (G) (Section 6), environment (E), and G x E interactions, therefore genetic variability provides an opportunity to reduce the concentration of Cd in the edible portions of the crops produced through development of low-Cd cultivars (Clarke et al., 1997b; Grant et al., 2008). The genetic potential for Cd accumulation in the edible portion of a crop can be manipulated through traditional genetic selection and plant breeding techniques, marker-assisted molecular breeding or genetic engineering. Initial surveys conducted to evaluate variation in Cd concentration of domestic Canadian cultivars identified lines with significantly lower Cd concentration than the predominant commercial cultivar. Subsequent surveys of the durum germplasm identified further genetic variation in cultivars and lines in international nurseries. Grain Cd concentration was found to be controlled by a single dominant gene on chromosome 5B (Clarke et al., 1997a; Penner et al., 1995). Lines with the low-Cd train had restricted translocation of Cd from the root to the shoot, which limited Cd accumulation in the grain and reduced grain Cd concentration by about 50% as compared to high-Cd lines. The low-Cd trait was highly heritable, so selection on a single plant basis was possible. A dominant random amplified polymorphic DNA marker (*OPC-20*) linked to the low-Cd gene was identified which aided in the development of low-Cd lines (Penner et al., 1995). Marker-assisted selection for low grain Cd has been used in the development of recent commercial Canadian durum wheat cultivars, which contain Cd levels about half of those in the high-Cd cultivars grown before the initiation of the low-Cd breeding program (Clarke et al., 1997a,b, 2010; Randhawa et al., 2013). In barley, a Sukkula-like transposable element inserted in the promoter region of *HvHMA3* gene was found to upregulate the expression of the gene, and introgression of this element into an elite barley cultivar through marker-assisted backcrossing resulted in a substantial decrease in grain Cd concentration without yield penalty (Lei et al., 2020).

Breeding programs have also been initiated to develop low-Cd rice cultivars. As with durum wheat, a number of QTLs have been reported for rice grain Cd concentration as discussed in Section 6 (Abe et al., 2013; Ishikawa et al., 2010; Norton et al., 2010; Ueno et al., 2009; Yan et al., 2019; Yang et al., 2018a), among which QTLs on chromosomes 3 and 7 (*q*Cd3 and *qCd7*) have been identified as *OsCd1* (Yan et al., 2019) and *OsHMA3* (Miyadate et al., 2011; Sui et al., 2019; Ueno et al., 2010), respectively.

Strong alleles of *OsHMA3* are associated with generally low Cd accumulation in the grain, whereas weak or null alleles of this gene produce high grain Cd concentration. Rice cultivars of the Indica subspecies generally accumulate higher levels of Cd in the grains than those of the Japonica cultivars (Arao and Ae, 2003; Sun et al., 2016; Yan et al., 2019; Yang et al., 2018a). This difference is possibly related to the natural variations in *OsHMA3* (Liu et al., 2020) and *OsCd1* (Yan et al., 2019) among the two subspecies. Strong alleles of *OsHMA3* have been identified in a number of rice cultivars, such as Nipponbare, which is a model cultivar widely used for molecular genetics studies (Yan et al., 2016). By introgressing *qCd7* from Nipponbare to Indica rice hybrids, grain Cd concentration was reduced by about 50% (Zhou et al., 2019). Similarly, differences in Cd transport activity between *OsCd1* alleles can also be explored. By introgressing the weaker $OsCd1^{V449}$ allele from Nipponbare into an Indica rice cultivar, grain Cd concentration was reduced by approximately 20% (Yan et al., 2019). Recent identifications of *GmHMA3* and *BrHMA3* alleles affecting Cd accumulation in soybean seeds and *Brassica rapa* leaves, respectively, will also allow marker-assisted breeding of these two important crops for low Cd accumulation (Wang et al., 2012; Zhang et al., 2019). In addition, existing cultivars possessing weak or null alleles of *HMA3*, likely to be high Cd accumulating, can be easily screened out of the breeding program based on molecular markers designed for the specific *HMA3* sequences. Low-Cd *OsNRAMP5* mutants of rice generated by ion-beam irradiation can also be used as a parental line in the breeding of low-Cd rice cultivars (Ishikawa et al., 2012). The mutated *OsNRAMP5* gene can be easily identified in the breeding program using appropriate molecular markers.

While traditional and marker-assisted breeding techniques can reduce grain Cd concentration, the magnitude of reduction may not be large enough to ensure compliance with food Cd limits, particularly when soils are contaminated. Genetic engineering can offer highly effective strategies to reduce Cd accumulation. One example is to knockout *OsNRAMP5*, which is responsible for the majority of Cd and Mn uptake by rice roots, using CRISPR/Cas9 gene editing technology. This has been done to both parental lines of a rice hybrid, producing hybrid rice with grain Cd concentration <10% of the concentrations in the wild type when grown on a contaminated paddy soils, to produce grain well below the food Cd limit (Tang et al., 2017a). Manganese uptake in gene-edited hybrid rice was also decreased markedly, but this did not appear to affect plant growth and grain yield, probably because Mn availability was high in the flooded paddy soil. In low Mn soils, knockout of *NRAMP5* may cause Mn deficiency and yield losses. The second example is to overexpress a functional allele of *OsHMA3* to enhance Cd sequestration in the root vacuoles. This approach has been done on both Japonica and Indica cultivars of rice, producing dramatic decreases (>90% reduction) in grain Cd concentration with little effects on grain yield or the concentrations of essential trace elements (Lu et al., 2019; Sasaki et al., 2014; Ueno et al., 2010). Knocking out of *OsLCT1* by CRISPR/Cas9 gene editing may be another approach to reduce Cd accumulation in rice grain (Uraguchi et al., 2011). Although transgenic approaches are highly effective, genetically modified crops need to be approved by government agencies and accepted by the public.

7.6 Reducing solubility/bioavailability of soil cadmium

7.6.1 Modifying soil pH—Liming

Soil pH is one of the major soil factors influencing Cd availability (Helmke, 1999). Solubility and hence plant availability of Cd in soils is closely related to soil pH (He and Singh, 1993b; Muhammad et al., 2012; Singh et al., 1995), with Cd availability decreasing as soil pH increases. As discussed in Section 4, Cd adsorption increases and Cd activity in the soil solution declines as soil pH increases (Bolan et al., 2003; Holm et al., 2003; Naidu et al., 1994; Tiller et al., 1979). Using data from 70 studies, 50% of the overall variation in soil Cd K_d could be explained by pH (Sauvé et al., 2000a, 2000b). In some areas in southern China, large proportions of rice grain samples exceeded the maximum permissible limit for Cd concentration ($0.2\,\text{mg}\,\text{kg}^{-1}$) (e.g. Chen et al., 2018a; Wang et al., 2019; Zhu et al., 2016). An important reason for the high Cd accumulation is soil acidification caused by the inefficient use of nitrogen fertilizers (urea or ammonium-based) (Zhao et al., 2015; Zhu et al., 2016). For example, in a large scale study of Zhu et al. (2016), median pH in paddy soils has decreased by almost one unit over the last 3 decades.

Other factors remaining constant, there is generally an inverse relationship between soil pH and plant accumulation of Cd (Andersson and Siman, 1991; Eriksson et al., 1996; Liu et al., 2015; Muhammad et al., 2012). In studies conducted across fields in southern Norway, there was a strong negative relationship between soil pH and Cd concentration in grasses (He and Singh, 1993b). Oat grain Cd concentration decreased with increasing pH in the range of 4.7–7.3 across fields in Sweden, with the effect being greatest in sandy rather than clayey soils (Eriksson et al., 1990). Similarly Cd concentration in rice grain (Yu et al., 2016) and wheat grain (Liu et al., 2015) was also negatively related to soil pH. In both biosolid-amended and non-amended soils, uptake of Cd by Swiss chard and lettuce was negatively related to soil pH (McBride, 2002). In a large scale paired rice grain and soil survey in southern China ($n=39642$), the median Cd transfer factor (i.e. grain Cd concentration/total soil Cd concentration) increased by 10-fold when soil pH decreased from 7.0 to 5.0 (Zhu et al., 2016).

Increasing the pH of acid soils through lime application can be effective in reducing Cd concentration of crops, particularly in pot trials and with highly contaminated or spiked soils. In container trials located in paddy fields using slightly Cd-contaminated soils, increasing pH from 6.4 to approximately 8.2 by application of dolomite or agricultural lime reduced Cd concentrations in rice grain sixfold from approximately $0.2\,\mathrm{mg\,kg^{-1}}$ to well below $0.05\,\mathrm{mg\,kg^{-1}}$ (Kim et al., 2016). Similarly, on a contaminated paddy soil, liming to increase pH from 5.8 to 6.1 decreased the Cd concentration in brown rice from $0.63\,\mathrm{mg\,kg^{-1}}$ in the control to $0.43\,\mathrm{mg\,kg^{-1}}$ (Duan et al., 2018), while other field studies liming a soil from its initial pH of 5.5–6.5 decreased Cd concentration of rice by 70%–80% (Chen et al., 2018b). In pot studies using soils collected from a long-term field trial that had been treated with lime to create pH ranging from 5.2 to 6.1, Cd uptake by wheat was reduced at higher pH levels (Chaudhary et al., 2011). In field studies, Cd concentration of carrot and Chinese cabbage was lower when soil pH was adjusted from 6.0 to 6.5 with lime as compared to pH reduction from 6.0 to 5.5 with application of sulfuric acid (Guttormsen et al., 1995). In a greenhouse study, concentration of Cd in carrot, spinach, oat and ryegrass decreased when pH was increased in a sandy soil (He and Singh, 1995). Greenhouse studies with potatoes showed that liming increased soil pH and reduced tuber Cd in potatoes (Maier et al., 2002b). In field experiments in Australia, increasing soil pH from 4.0 to 5.0 with lime application generally resulted in a decrease in Cd concentration in barley and wheat grain, with part of the effect at several sites due to dilution from increased grain yield at higher soil pH (Oliver et al., 1996).

While liming has been proposed as a management practice to reduce Cd and can frequently decrease Cd concentration of crops, the effect is not necessarily consistent and may vary with crop type. In pot studies, liming to increase pH from 4 to 7 exponentially reduced Cd concentration of winter rape, but Cd concentration of ryegrass increased when pH was increased to 6, then declined when pH was further increased to 7 (Eriksson, 1989). On a naturally Cd-rich alum shale, Cd concentration of wheat and carrot was reduced substantially when pH was raised from 5.5 to 7.5, but Cd concentration of lettuce was not affected (Singh et al., 1995). Liming acid biosolids-amended soils to a neutral pH reduced Cd concentration in lettuce and cabbage, but not in potato tubers (Jackson and Alloway, 1991). Cadmium concentration in potatoes, oat straw and ryegrass grown on biosolid-amended fields decreased as pH was increased through lime application along the range from 3.9 to 7.6, but Cd concentration of oat grain was not affected (Smith, 1994).

Many of the large benefits of liming on Cd concentration have occurred in pot studies, where the soil around the roots can be uniformly treated. Liming may be less effective under field conditions where liming will predominately affect the surface soil, so crops may absorb Cd from soil layers where the pH is unaffected (Li et al., 1996). In pot studies, lime application to acid soils reduced concentration in potato tubers, while current season application of lime in field locations (on the same soils) had no significant effect (Maier et al., 2002a). At several field sites, increasing pH from original levels of 5.9–6.5 to levels of 7.0–7.5 after lime application did not reduce Cd concentrations of sunflower kernels possibly because the deep-rooted sunflower accessed Cd from unamended soil depths (Li et al., 1996). In field experiments with potatoes on soils with initial pH ranging 5.1–6.1 liming decreased surface soil pH but did not reduce Cd concentrations in tubers (Oborn et al., 1995; Oborn and Jansson, 1998; Sparrow et al., 1993b). However, when potatoes and carrots were planted two to 5 years after lime application, Cd concentrations in the potato tubers and carrot roots were reduced, likely because soil mixing during the potato harvest moved the lime more deeply in the soil (Sparrow and Salardini, 1997). On some soils, the effect of liming may also dissipate relatively quickly. In Australian studies, Cd concentrations in wheat grain on 3 of 8 sites and in barley on one of the 8 sites was reduced only in the year of lime application and not in subsequent years (Oliver et al., 1996). In a field trial lasting 3 years, one-time application of lime (calcium carbonate) was effective at reducing rice grain Cd concentrations in all three seasons (Chen et al., 2018a; Wang et al., 2019).

Liming would not be expected to be effective on neutral to alkaline soils. In pot studies using five soils, lime application tended to reduce Cd concentrations in lettuce grown on three acid soils, but not on the higher pH soils (Maclean, 1976). In field studies, increasing pH from original levels of 5.9–6.5 to levels of 7.0–7.5 after lime application did not reduce Cd concentrations of sunflower kernels possibly because the soils were not initially very acidic (Li et al., 1996). In some situations, addition of lime and gypsum has increased plant uptake of Cd due to the exchange of the Ca with the Cd, leading to an increase in Cd concentration in the soil solution (Bolan et al., 2003; Eriksson, 1989; Williams and David, 1976). In pot studies, Cd concentrations in ryegrass increased with increasing pH in a loam soil, possibly because of the Ca supplied though the lime application (He and Singh, 1995). On soils that had a high Cd:Zn ratio due to application of Cd-enriched biosolids, lime-induced Zn deficiency may have contributed to increased Cd concentrations in lettuce (Chaney et al., 2006). Similar results were seen in pot studies using shale soils with a naturally high Cd: Zn ratio where increasing soil pH to 7.9 decreased Zn and increased Cd concentrations in lettuce (Chaney et al., 2009). Liming was shown to reduce the availability of Zn, Fe and Mn, leading to the upregulation of genes involve in the uptake of these elements which could lead to an increase in Cd accumulation under some circumstances (Yang et al., 2018b).

While lime application may reduce Cd concentration in crops grown on acid soils, its benefits may vary with crop type, soil characteristics and environmental conditions. Therefore, while it should be considered as a practice for Cd reduction, its effectiveness may vary and should be evaluated on a site-by-site basis. Under situations where crop yield increases occur due to lime application, reductions in Cd may be a co-benefit.

7.6.2 Immobilization and sorbents

In situ immobilization can be used to reduce availability of Cd in contaminated sites. Immobilization will remove Cd from the soil solution through reactions such as precipitation, complexation and adsorption, thus reducing its phytoavailability (Bolan et al., 2014). In some cases, availability is decreased through increased soil pH, as discussed above (Section 7.6.1). A wide range of substances including zeolites, phosphate, as well as organic materials such as biosolids, biochars and humic acids have been evaluated for their ability to reduce Cd availability on polluted soils (Guo et al., 2006; Mahar et al., 2015).

7.6.2.1 Inorganic sorbents

Applications of very high rates of P, above those normally used for crop production, can immobilize Cd by P-induced Cd^{2+} adsorption and/or precipitation of Cd (Bolan et al., 2014; Bolan and Duraisamy, 2003; Kunhikrishnan et al., 2018; McGowen et al., 2001). The increased adsorption could be related to increased surface charge, co-adsorption of P and Cd as an ion pair or surface complex formation of Cd on the P compound. Both water-soluble forms of P such as DAP and relatively insoluble forms of phosphate such as apatites or phosphate rock have been shown to immobilize Cd in highly contaminated soils (Bolan et al., 2014). While possibly effective as a management practice on highly contaminated soils, immobilization using high P rates would not normally be considered as an economically viable practice on soils in broad-acre agriculture having lower Cd concentrations.

Red mud, a by-product of the aluminum industry, formed during the digestion of bauxite and caustic soda can also be used to increase soil pH and encourage Cd sorption (Bolan et al., 2014; Garau et al., 2007). The Fe and Al oxides present in red mud may also contribute to Cd fixation (Lombi et al., 2002b) as metal oxides have been shown to sorb and immobilize a range of contaminants (Bolan et al., 2014). In pot studies on contaminated soils, application of red mud increased crop growth and reduced Cd concentration through three crop cycles (Lombi et al., 2002b). Other alkaline industrial by-products such as wood ash may also reduce Cd uptake through their effects on soil pH, although there is concern about the addition of Cd that is concentrated in the wood ash after burning (Section 2.2.6).

Zeolites are a class of porous alumino-silicates with a negative charge that can be used to sorb Cd (Garau et al., 2007). Zeolites will vary considerably in their structure and exchange capacity depending on their origin, but in many studies have been shown to reduce phytoavailability of Cd. In pot studies on soils spiked with high concentrations of Cd as $CdCl_2$, zeolite was effective at reducing Cd accumulation in *Chamomilla recutita* (Grejtovský et al., 1998). Zeolites were also effective at reducing Cd uptake from spiked soils in pot studies with barley and maize (Chlopecka and Adriano, 1997). Pot studies on contaminated soils showed that zeolites and Fe oxides or hydroxides were effective in reducing Cd phytoavailability (Gworek, 1992; Mench et al., 1994). Other pot studies using contaminated soils showed that zeolites were effective at reducing Cd uptake by white lupin (Castaldi et al., 2005).

Beringite, a modified aluminosilicate by-product from the burning of coal refuse from a coal mine in Belgium (Berigen), has been used to reduce Cd accumulation in plants (Oste et al., 2001) while combining beringite with compost and using metal tolerant crops was effective in regeneration of a metal-contaminated site (Vangronsveld et al., 1995). Beringite was also effective in reducing Cd accumulation through three crop cycles in pot studies on contaminated soils (Lombi et al., 2002b).

While there is evidence in the literature that many of these sorbents appear to work in highly contaminated soils and in pot trials, there is less evidence that they can economically be used to reduce crop Cd concentration at a wide scale commercially in agricultural fields.

7.6.2.2 Organic materials

Organic materials such as animal manures, biosolids, composts, peats or other organic waste products may influence Cd availability. In field studies, addition of peat to soils reduced extractable Cd, especially on soils that were originally low in organic matter (Eriksson, 1990). Peat addition also decreased Cd uptake by plants in the year of application but the effect did not persist to the second or third year of cropping (He and Singh, 1993a; Singh and Myhr, 1998).

Use of waste materials that have the capacity to reduce Cd availability may be attractive if the materials are low cost and their diversion from the waste stream is beneficial. In addition, some of these organic waste materials including manure, biosolids and other organic by-products have additional benefits in providing a slow release source of nutrients and improving soil structure.

Application of livestock manure can either increase or decrease Cd availability. Animal manures may contain Cd as a contaminant, and annual application of fresh manure since 1850 in studies at Rothamsted increased soil Cd concentrations as compared to untreated or P-treated plots. The N and organic acids present in manures may also lower soil pH and mobilize Cd (Jones and Johnston, 1989). However, insoluble organic complexes with Cd may form as the manure decomposes, reducing Cd availability for plant uptake (Jones and Johnston, 1989). Manures may also contain high concentrations of Zn used as antimicrobial feed additives, and this may provide additional benefits in terms of reducing Cd uptake. Addition of animal manure and peat to polluted soils enhanced the mobility of heavy metals at lower pH values and decreased it at higher pH (Ram and Verloo, 1985a) while other pot studies on contaminated soils showed that additions of manure decreased Cd concentration and uptake of corn (Ram and Verloo, 1985b). Therefore, the effect of manure on Cd phytoavailability will depend on the soil characteristics and other environmental and management conditions.

Large amounts of biosolids can be added to agricultural lands, especially near urban centers and can be a considerable source of Cd input (Sheppard et al., 2009). Establishment and enforcement of limits of Cd in biosolid application (Section 1.3) are important to prevent the accumulation of excess Cd in agricultural soils. However, biosolids are also a source of organic matter that can stabilize Cd in the soil, especially if the biosolids have received alkaline treatments. Biosolids may also contain Zn, which can compete with Cd for root uptake or phloem loading in the plant (Section 7.3). Stabilized biosolids that are low in Cd may reduce the bioavailability of Cd in contaminated soil (Bolan et al., 2014). A limed biosolid compost was very effective at reducing Cd accumulation in turfgrass in field studies on a highly contaminated site (Li et al., 2000).

Other organic wastes have also been evaluated for effects on Cd availability. Application of tobacco dust, grape marc and mushroom compost in a 6-month pot incubation trial increased soil organic matter but the grape marc and tobacco dust decreased soil pH (Karaca, 2004). The decrease in soil pH with the tobacco dust was correlated with an increase in DTPA-extractable Cd. However, mushroom compost and grape marc decreased DTPA-extractable Cd. Similarly, application of compost was effective at reducing Cd uptake by white lupin (Castaldi et al., 2005).

A range of humic substances, many of which are by-products of coal mining, are readily available and may immobilize Cd in soils. Alkaline humic adsorbents produced from leonardite immobilized Cd in contaminated soils in incubation studies (Meng et al., 2017). In pot studies on soils spiked with high concentrations of Cd as $CdCl_2$, lignite was effective at reducing Cd accumulation in *Chamomilla recutita* (Grejtovský et al., 1998). Lignite also reduced Cd uptake by ryegrass in pot studies using pasture soils, with the effect being stronger in low- than high pH soils (Simmler et al., 2013).

Biochar is a solid product of pyrolysis and is considered an effective sorbent. Biochar can contain very high concentrations of organic carbon that is stable in the soil and can have beneficial effects on soil physical and chemical characterizes (Atkinson et al., 2010). Sorption of Cd on the large surface area of biochars can reduce the concentration of Cd present in the soil solution and may reduce its mobility in contaminated soils (Beesley and Marmiroli, 2011). In a pot study using Cd-contaminated soils, biochar derived from the pyrolysis of sugar cane residue increased soil pH and reduced DPTA-extractable Cd and Cd concentrations in jack beans and *Mucuna aterrima* (Puga et al., 2015). Other pot studies with contaminated soils showed that biochar application decreased Cd concentration in pore water and decreased phytotoxicity of the soil for emergence of *Lolium perenne* L. (Beesley et al., 2010). Cadmium concentration in maize tissue was reduced by biochar application in pot studies using contaminated soils

(Al-Wabel et al., 2015). Field experiments have shown that applications of biochar can decrease Cd accumulation in rice grain, and the effect can be attributed mainly to increased soil pH (Bian et al., 2013, 2014). As large amounts of biochar ($>20\,\mathrm{t\,ha^{-1}}$) are needed, the cost would be much higher than liming.

Similar to inorganic sorbents, the effectiveness of using large amounts of organic materials to sorb Cd in agricultural soils is rarely demonstrated in the field on agricultural soils. However, the economics of organic wastes are probably more favorable than inorganic sorbents and availability of materials is likely to be more widespread. It should also be noted that adding large quantities of organic wastes to soils may cause other problems—increasing risks of ammonia toxicity, nitrate leaching, or P runoff.

7.6.3 Salinity control

Salinity can have a major effect on crop Cd concentration. Saline soils are characterized by the presence of elevated soluble salts, normally the chloride and sulfate salts of Ca, magnesium and sodium, which leads to a high soil solution osmotic potential. Soil salinity can depress crop growth which can indirectly increase plant Cd concentration through dilution/concentration effects. However, soil salinity can also influence Cd concentration directly by effects on the solubility and mobility of Cd in the soil solution (Section 3.1.2). Increasing ionic strength of the soil solution can decrease Cd adsorption and increase Cd concentration in the solution (Naidu et al., 1994). Cadmium availability is also affected by the presence of other ions in the soil solution as described in Section 4. In particular, Cd will form moderately stable complexes with Cl^-, including $CdCl^+$ and $CdCl_2^0$ when the Cl− concentration in the soil solution rises to levels commonly found in saline soils (Ghallab and Usman, 2007; Smolders et al., 1998; Smolders and McLaughlin, 1996a,b). Despite chlorocomplexes of Cd being less available for root uptake than the free Cd^{2+} ion (Smolders and McLaughlin, 1996b), formation of these complexes can increase plant accumulation of Cd by increasing the diffusion of Cd through the soil to the plant root (Degryse et al., 2006; Smolders et al., 1998; Verheyen et al., 2012). Under field conditions, elevated Cl− levels increased Cd uptake in potatoes (McLaughlin et al., 1994a, 1997a) and sunflower (Li et al., 1994). Field studies in North Dakota showed that concentration of Cd in durum wheat grain increased curvilinearly with increasing soil Cl^- (Norvell et al., 2000). Rate of increase of grain Cd was greatest at lower concentrations of Cl^- associated with relatively minor salinity. Sulfate ions will also form soluble complexes with Cd and may increase Cd uptake by plants to some extent but do not have the same marked effect on Cd diffusion and plant availability as chloro-Cd complexes (López-Chuken and Young, 2010; McLaughlin et al., 1998a,b).

The effect of salinity on increasing Cd uptake in plants may be particularly important under irrigation. Irrigation is often used in high value crops, combined with intensive applications of fertilizers and soil amendments that may contain Cd. Irrigation water may contain significant amounts of Cl^- and/or SO_4^{2-}. For example, in potato fields that showed elevated Cd concentrations in the crop, irrigation water had electrical conductivity in the range of 2.5–3.5 $dS\,m^{-1}$ with Cl^- concentrations in the range of 11–34 mM (McLaughlin et al., 1999). Loss of water from the field through crop use and evapotranspiration increased the concentration of Cl^- in the soil solution. Under these conditions, $CdCl_n^{2-n}$ complex may dominate the Cd solution chemistry, leading to enhanced Cd uptake by crops (McLaughlin et al., 1997b).

If producers have a choice of irrigation water sources, selection of higher quality irrigation water containing lower concentrations of Cl^- can help to reduce crop Cd concentrations. However, producers are generally restricted in their choice of water supplies. General methods for control of salinity under irrigation include using drip irrigation to reduce negative effects of salinity by keeping soil around the plant roots moist and provide steady leaching of salts to the outside of the wetted area. In well-drained, sandy soils, adding high amounts of irrigation water in excess of crop use can be used to flush salts below the rooting zone. Frequent light irrigations especially during hot, dry conditions where evaporation is high will increase the concentration of salt in the soil solution and should be avoided. If Cl^--based salinity is a concern, fertilizers that contain Cl^-, such as KCl should be avoided. Application of waste materials high in Cl^- to soil should also be avoided (Dahlin et al., 2016). If irrigation water is high in Cl^-, it is likely that Cd uptake will be enhanced regardless of the management practices and irrigation method used. Therefore, selection of crop species or cultivars that are genetically low in Cd accumulation should be considered.

Dryland Cl^--based salinity will also encourage crop uptake of Cd (Li et al., 1994). In dryland agricultural systems, soil salinization can occur when water use by the crop is not well-matched with water availability because of fallowing or the production of shallow-rooted annual crops. The unused water from excess precipitation can move below the rooting zone as recharge carrying dissolved salts to the water table. The water table may rise or groundwater can flow to low-lying areas where the water moves by capillary flow to the soil surface still carrying the salts which accumulate in the rooting zone as the water evaporates. In areas of high rainfall, the water can be flushed from the soil through infiltration and leaching, but in more arid zones or in dry years, the salts will accumulate because rainfall infiltration is insufficient to leach the salts from the rooting zone. Management of dryland salinity is problematic and includes matching water use with water supply. Practices include avoiding summer fallow in favor of continuous cropping using annual crops with water demand matched to water supply or planting perennial crops or tree crops with high water demand. Deep-rooted barrier crops may be planted to intercept water moving from recharge to discharge areas. Strategic surface and subsurface drainage may be used to improve water distribution in the landscape. In areas where Cl^--based salinity is a concern, production of crop species or cultivars that are genetically low in Cd may be required.

7.7 Macronutrient fertilizers

Fertilizer application can influence Cd both directly through addition of Cd present in the fertilizer and indirectly through effect on soil chemistry, microbiology and plant growth. The former have already been discussed in Section 2.2.2, while the latter are discussed below. Fertilizer effects may occur in the year of application or through fertilizer-induced long-term changes in soil conditions.

7.7.1 Long-term effects of phosphorus fertilization

Effects of long-term P fertilization on the soil-plant system may also influence Cd availability. As described previously, Cd availability is affected by a range of factors including soil pH, type and content of organic matter, CEC and complex formation. Many of these factors may be influenced by long-term application of P fertilizers. Nitrification of the ammonium portion of compound phosphate fertilizers such as MAP or DAP will release H^+ ions, leading to some degree of acidification (Kennedy, 1986). At commercially relevant rates of application, MAP was shown to decrease soil pH in both laboratory and field studies, with the magnitude of the decrease increasing with fertilizer application rate (François et al., 2009; Lambert et al., 2007).

With repeated fertilizer applications over time, accumulation of P and cumulative effects on pH may influence Cd availability, particularly on poorly buffered soils. In addition to Cd, P fertilizers may also contain Zn as an impurity, at concentrations ranging from 50 to over 3500 mg kg^{-1} (Lambert et al., 2007). As with the Cd, Zn may accumulate in the soil over time, if input is less than offtake increasing Zn concentrations in the soil solution (Lambert et al., 2007). Zinc and Cd are chemically similar and may compete for binding sites in the soil system and for uptake and translocation within the plant as described in Section 7.3. Therefore, the presence of Zn as a contaminant in P fertilizer may reduce Cd accumulation in crops. If P fertilizers are effective in increasing crop yield, they will also tend to increase the amount of crop residues, roots and exudates returned to the soil which may increase soil OM levels (Campbell et al., 1991; Janzen et al., 1998; Schjønning et al., 1994). Changes in OM content of soils may influence Cd availability (Eriksson et al., 1990; He and Singh, 1993a) although studies directly assessing the influence of changes in OM content caused by fertilization on Cd accumulation in crops are lacking.

7.7.2 Fertilizer effects in the year of application

While the long-term effects of fertilizers on soil properties and Cd accumulation are of concern, the effects of fertilizers in the year of application may also be important. Fertilizers will have an immediate effect on the ionic strength, composition and pH of the soil solution as well as on crop growth, root distribution and rhizosphere chemistry. The immediate direct and indirect effects of fertilization on soils and crops can influence Cd availability and crop accumulation and concentration. Dilution/concentration effects may influence Cd concentration in crops if fertilizers affect crop biomass production in the absence of effects on Cd phytoavailability. The net effect of fertilization on Cd concentrations in crops will be influenced by crop type, soil characteristics and fertilizer rate, source, timing and placement.

7.7.2.1 Phosphorus

The effect of P fertilizer on Cd concentrations in plants will depend not only on the Cd concentration of the fertilizer but also on the specific fertilizer characteristics. Short-term availability of the Cd in P fertilizers will depend greatly on the solubility of Cd in the fertilizer. The amount of Cd measured by DTPA extraction after incubation of the fertilizer and the release of Cd in sequential extractions was higher from soluble TSP than from relatively insoluble rock phosphate (Kuo et al., 2007). Under greenhouse conditions, application of NPK fertilizer containing 417 mg Cd kg^{-1} P increased the Cd concentrations in carrots (*Daucus carota* L.), lettuce (*Latuca sativa* L.), oat

(*Avena sativa* L.) and ryegrass (*Lolium multiflorum* L.) while a low-solubility rock phosphate containing a similar Cd concentration had no effect (He and Singh, 1995).

Phosphate fertilizer may also influence plant Cd concentrations through effects on ionic strength, soil pH, and crop growth. In growth chamber studies, Cd concentrations in flax and durum wheat were increased by MAP and TSP, even when reagent grade forms were used that did not contain significant amounts of Cd (Jiao et al., 2004). In field studies in Australia, Cd concentrations of field-grown potato tubers (*Solanum tuberosum* L.) increased with application of double superphosphate but were not greatly affected by the concentrations of Cd in the fertilizers used (Sparrow et al., 1993a). Similarly field studies on the Canadian Prairies, Cd concentrations in durum wheat (*Triticum turgidum* L.) increased with application of recommended rates of MAP fertilizer, but were generally unaffected by the concentration of Cd in the fertilizer (Grant et al., 2002) unless the rate of application was increased beyond normally recommended levels (Grant et al., 2013).

Different P sources may affect Cd differently because of their effects on soil pH and ionic strength. Uptake of Cd by rape and oats in pot studies was higher with single superphosphate that with an NPK blend with similar Cd concentration, possibly because of acidification from the single superphosphate (Singh, 1990). Laboratory adsorption studies showed that addition of MAP decreased soil pH and reduced the amount of Cd adsorbed by soils while addition of DAP increased soil pH and reduced Cd availability (Levi-Minzi and Petruzzelli, 1984). However, it is unlikely that agronomic rates of application would have as great an effect on Cd as the large applications reported. Under field conditions, using agronomically relevant rates of application, there was little observed difference among single superphosphate, reactive phosphate rock, MAP and DAP in their effects on Cd concentrations in potato tubers (McLaughlin et al., 1995).

Placement of P fertilizer may also influence Cd accumulation in crops. Placing the fertilizer in a concentrated band creates a micro-region with very high ionic strength, reduced pH and enhanced root development. Under field conditions, Cd concentrations in potato tubers were increased more with banded rather than broadcast application of TSP (Sparrow et al., 1992). Cadmium concentrations in flax were increased more with banded than broadcast MAP (Grant and Bailey, 1997) while banding occasionally, but not consistently, led to higher grain Cd concentrations in durum wheat (Grant and Bailey, 1998).

Under field conditions, fertilizers may have a smaller effect on crop Cd concentrations than in greenhouse studies because plant roots under field conditions can explore a larger soil volume that is less affected by the P addition than in confined pots. Under field conditions, accumulation of Cd in cabbage was not affected by Cd applied in NPK fertilizer (Guttormsen et al., 1995). Cadmium concentrations in barley were not affected by Cd applied in NPK fertilizers in the year of application under field conditions (Singh and Myhr, 1998). In Australian field studies, Cd concentrations in potato tubers were not affected by the Cd concentration in band application of single superphosphate, reactive phosphate rock, MAP and DAP containing high or low Cd concentrations (McLaughlin et al., 1995).

7.7.2.2 Nitrogen

Cadmium concentrations in crops have been shown to increase with applications of N fertilizers at agronomically relevant rates of application although N fertilizers do not normally contain significant amounts of Cd (Andersson, 1976; Brown et al., 1994; Eriksson, 1990; Grant et al., 1996; Grant and Bailey, 1998; Kashem and Singh, 2002; Li et al., 2011; Mitchell et al., 2000; Perilli et al., 2010). Nitrogen fertilizer may increase plant-available Cd due to a fertilizer-induced reduction in soil pH. Nitrogen fertilizers containing ammonium-N can acidify the soil and decrease rhizosphere pH (Eriksson, 1990; Florijn et al., 1992; Mitchell et al., 2000). Fertilizer-induced pH changes may be of particular importance on poorly buffered soils and on soils where pH is below 7.0. However, changes in rhizosphere pH may be important regardless of effects on the bulk soil. In hydroponic and pot studies, ammonium nutrition of sunflowers increased proton extrusion from the root reducing rhizosphere pH irrespective of the initial soil pH (Zaccheo et al., 2006).

Effects of N fertilization are not only due to pH changes. The ammonium ion can also desorb Cd from exchange sites or soil colloids *via* ion exchange increasing plant-available Cd in the soil solution (Lorenz et al., 1994). In pot studies, Cd concentrations of water spinach (*Ipomoea aquatica* L.), radish and oat (*Avena sativa* L.) increased with N fertilization, although pH was not decreased (Kashem and Singh, 2002). In pot studies with durum wheat, grain Cd concentration increased with N fertilization in the order $Ca(NO_3)_2 = \text{urea} > (NH_4)_2SO_4$, with the increase unrelated to the pH effects of the fertilizers (Brown et al., 1994). The Ca^{2+} in the $Ca(NO_3)_2$ may have replaced bound Cd^{2+}, increasing the soil solution

Cd concentration. In pot studies, both the Cd in soil water displaced from the entire soil volume of the pot and Cd concentration of durum wheat increased with application of urea (Mitchell et al., 2000). The soil solution pH was not affected by the urea application over the 40 days of the study period, but the electrical conductivity of the solution increased with increasing N application, indicating that the increased osmotic strength of the soil solution contributed to the higher phytoavailable Cd. The effect of N source on the phytoavailability of Cd will be influenced by the initial pH of the soil and its buffering capacity.

Fertilization effects are likely to be greater in pot studies where root volume is restricted than under field conditions, but crop Cd concentrations have also been shown to increase with N applications in field studies (Eriksson, 1990; Gao et al., 2010; Grant et al., 1996; Grant and Bailey, 1998; Maier et al., 2002b; Perilli et al., 2010; Wångstrand et al., 2007). Nitrogen placement may also influence plant response, as placement of N in a concentrated band will lead to a small volume of soil where effects on Cd solubility and mobility may be greater than in the bulk soil. If N and P are banded together, the N may influence the solubility of the Cd added in the fertilizer P. Growth chamber studies showed lower concentrations of Cd in durum wheat when urea was banded as compared to mixed thoroughly with the soil (Brown, 1997; Brown et al., 1994). However, field studies showed no consistent effects of urea placement on Cd concentrations in durum wheat (Grant and Bailey, 1998).

7.7.2.3 Potassium

Potassium fertilizers may also influence Cd availability to crops, through effects on plant growth, soil pH, ionic strength of the soil solution complexation, and/or ion competition (Grant et al., 1996). Under field conditions, KCl increased Cd concentrations in barley (Grant et al., 1996). The accompanying ion in the potassium fertilizer may have a strong effect on Cd availability. In pot studies with spring wheat, Cd accumulation and concentrations in plant shoots increased with increasing application rates of KCl and potassium sulfate (K_2SO_4) from 0 to 166 mg K kg^{-1} with no significant differences occurring between the two K sources (Zhao et al., 2004). However, shoot Cd concentrations were lower with KNO_3 than with KCl or K_2SO_4 and were only increased by the highest rate of KNO_3 application. In fields studies in Tasmania, Cd concentrations in potato tubers were higher with KCl application than with K_2SO_4 (Sparrow et al., 1994). As discussed in Section 3.1.2, Cl^- will increase the availability of

Cd in soils through formation of chlorocomplexes (Smolders et al., 1998; Smolders and McLaughlin, 1996a,b). Therefore, application of Cl^- in KCl fertilizers may play an important role in its effect on Cd availability.

8. Conclusions and outlook

While there is much scientific debate regarding the level of risk posed by Cd in the food chain, the deliberations of the FAO/WHO JECFA represent the broad international consensus of human health specialists on food chain Cd risks. That committee recently examined the tolerable intakes for Cd and slightly reduced the provisional tolerable monthly intake to $25\,\mu g\,kg^{-1}$ body weight. Other jurisdictions (e.g. the EU) have determined that human intakes need to be controlled to lower levels. Hence, pressure will continue to bear on agriculture to meet food Cd regulations that may become stricter in the future. The trend for higher human Cd intakes over time in some countries (e.g. China) is cause for concern and requires a focus on developing methods to mitigate Cd transfer through the food chain, and limits to minimize further Cd contamination of soils. Furthermore, better estimates of mass balances of Cd in Chinese soils are needed, particularly quantifying inputs from the atmosphere and animal wastes. At a global level, more accurate estimates of Cd losses from topsoils by leaching are needed to better estimate the maximal rates of Cd loading to soil that would not lead to further accumulation in soils and the food chain.

There are a wide range of options for farmers to minimize Cd transfer from soils to crops, with great gains being made in understanding the genetics and physiology of Cd transfer from soil through roots to plant foods. Introduction of new low-Cd accumulating varieties is a simple agronomic tool for farmers to produce high quality (low Cd) crops, but often years of effort and considerable resources are required to develop and release such low-Cd cultivars. Other options to reduce transfer to foods require more intervention by farmers, usually related to addition of amelioration agents to soil or specific cultural practices, which may increase costs of production and therefore adoption is often harder to achieve. Where foods are regularly monitored for Cd quality and access to markets is reliant on meeting a particular food Cd standard, adoption is usually accelerated.

The effectiveness of various management interventions to control the entry of Cd into the food chain varies (Table 10). On the one hand, site selection, through the use of a predictive soil test to target soils with little

Table 10 Timeline for effectiveness of various agronomic/regulatory management interventions to control Cd concentrations in the food chain.

Management option	Timeline
Change cultivar	Rapid (1-2 years)
Change crop type	↓
Select low Cd risk soils	
Addition of Zn	
Adding sorbents	
Increase soil pH (liming)	
Breeding new low Cd cultivars	
Reducing soil salinity	
Reducing Cd inputs	Slow (decades)

bioavailable Cd, will have a significant and rapid effect on reducing food Cd concentrations. Reducing Cd limits in farm inputs, on the other hand, will take decades to have any effect on food Cd quality as crops will still have access to significant amount of Cd already present in soils (either from geogenic or anthropogenic sources). A timeline of the suggested effectiveness of interventions is shown in Table 10. While reducing Cd inputs, such as limiting Cd concentrations in fertilizers, may have little effect on crop Cd concentrations in the short term, this is no excuse for a lack of action. Allowing Cd to continually accumulate in soil could not be regarded as sustainable management of the soil resource as it just delays the time when food quality will be compromised. Determining the loadings of Cd to soil that do not allow excessive accumulation is a key research gap that relies on the difficult measurement of small leaching fluxes of Cd from soil under field conditions. At the same time, we need to recognize that Cd is a naturally occurring element and is present in all soils, agricultural or otherwise, and soils with high concentrations of geogenic Cd also need to be carefully managed; a clear example being the accumulation of Cd in cacao in South America where the young soils naturally contain high Cd concentrations. Agronomic practices coupled with the exploitation of genetic controls on Cd accumulation in foods as outlined in this review offer considerable scope for sound management of Cd in agricultural systems.

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